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CHAPTER 12

THE EXPLOSIVES INDUSTRY

by

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EXPLOSIVES INDUSTRY

INDUSTRY DESCRIPTION

The explosives industry as a whole includes companies which manufacture organic nitration products and formulate mixtures of chemicals with explosive properties. Some 135 chemicals or formulations which are useful as explosives have been identified. Seventy-five are used industrially in mining, quarrying, excavating, and loosening oil and gas formations; forty-five find primary application in military weapons, rockets, missiles and space vehicles; and fifteen are used for both purposes.

Explosives are defined as substances which undergo sudden, rapid self-propagating chemical transformations accompanied by evolution of large quantities of gas and/or heat which exert high pressures on surrounding media. They are characterized by their rate of transformation. Ease of initiation (sensitivity) and maximum explosive energy available for useful work (strength) are other important characteristics. Explosives are usually classified in two groups, low or deflagrating explosives and high or detonating explosives. Low explosives or propellants have a low burning rate when unconfined which never exceeds a few cm/sec. High explosives produce detonation waves with propagation velocities of 2-11 km/sec and exert great shattering action or brisance. High explosives are further categorized as primary or secondary according to their relative ease of initiation to detonation. The first group, known as primary or initiating explosives, consists of compounds sufficiently sensitive to heat, impact or friction to undergo explosive decomposition when subjected to such forces. These materials exhibit varying capacities for induction of detonation in less sensitive explosives. The second group, known as secondary or non-initiating high explosives, comprise the greater number of explosive compounds and are used on a large scale for military and industrial purposes. Secondary explosives require detonators (fuse caps) and/or boosters for detonation.

Manufacturing establishments in the explosives industry are classified in SIC Code 2892. This classification includes both commercial firms and government-owned plants operated by private firms. The latter are termed GOCO (government-owned/contractor-operated) plants. Government-owned/government-operated (GOGO) plants are not included in SIC Code 2892. Both commercial and military plants manufacture high explosives, propellants, and initiating compounds and perform formulating (load, assemble and pack) operations. The two types of establishments employ essentially the same production processes, but plant sizes, major products, end uses and factors affecting production rates differ. Commercial firms produce primarily ammonium nitrate based explosives, dynamites and nitroglycerin; TNT, HMX and RDX are primarily military explosives, and nitroglycerin and nitrocellulose are components of military propellants. In order to provide guidelines for limitations on waste-water effluent and atmospheric emissions, activities of the explosives industry have been categorized according to production process and product types. On this basis, industrial activities may be divided into four categories: A) Manufacture of Explosives, B) Manufacture of Propellants, C) Formulation (Load, Assemble and Pack [LAP]) Activities, and D) Manufacture of Initiating Compounds. Manufacture of explosives, propellants, and initiating compounds generally involves nitration of an organic molecule using nitric acid. Processes described in this chapter are limited to those involving organic nitration reactions, recovery and purification of the nitrated products and production of nitric acid. Six operations are included: Nitric Acid Production, TNT Production, Nitrocellulose Production, RDX/HMX Production, Nitroglycerine Production, and PETN Production. Actual propellant formulation or load, assemble and pack activities are not included in the process descriptions, although they occur at some of the facilities which conduct nitration operations. Figure 1, a schematic represenation of the explosives industry, is included to show this interrelationship.

Dry blasting agents, slurrys, and water gels account for over 80 percent of all explosives produced by the commercial explosives industry (privately owned and operated companies). These are formulated products of basic load, assemble and pack operations and contain ammonium nitrate as the primary ingredient. Ammonium nitrate production is described in Chapter 22, Phosphate Rock and Basic Fertilizer Materials. As stated previously, process descriptions for such formulating operations are not included in this chapter.

Data published in the 1972 Census of Manufacturers indicate there were 93 establishments classified in SIC Code 2892. These included establishments primarily engaged in manufacturing sporting powder, high explosives, nitrated carbohydrates, safety fuses and blasting and detonating caps. Not included were GOGO plants and establishments primarily engaged in small arms ammunition manufacture or shooting wells. The latter category includes some nitroglycerin manufacturers.

Seven of the 93 installations are GOCO plants; four of these are now inactive, leaving only three currently conducting nitration operations. Additional sources of information indicate that some 13 of the 86 commercial establishments in SIC Code 2892 also conduct nitration processes.

The commercial explosives industry sold 1.25 Tg (1.38 million tons) of products including blasting agents and fixed high explosives for consumption in 1973. Current military production data were not available in the sources consulted for this study. During the 1969-1971 production period the military explosives production rate was 518 Gg (571 thousand tons)/year, and the rate of production of acids including oleum, dilute and concentrated HNO_3, and concentrated H_2SO_4 approached 275 Gg (303 thousand tons)/month. Military production rates have decreased since the 1969-1971 production period. The literature indicates that explosives manufacturing plants vary in area from 1-10 km^2. Processing areas are generally isolated from each other to minimize the possibility of sympathetic detonation in the event of an explosion. Data on capacity variations were not found. Employment statistics for 1972 were available for establishments classified in SIC Code 2892. Seven GOCO plants employed 7,600 production workers and 86 privately-owned/privately-operated establishments employed 5,900 production workers. A few establishments employed more than a thousand employees.

Figure 2 illustrates geographic locations of both commercial and military manufacturing plants. Explosives plants are evenly distributed in the Eastern U.S., generally away from large population centers in rural or previously rural areas.

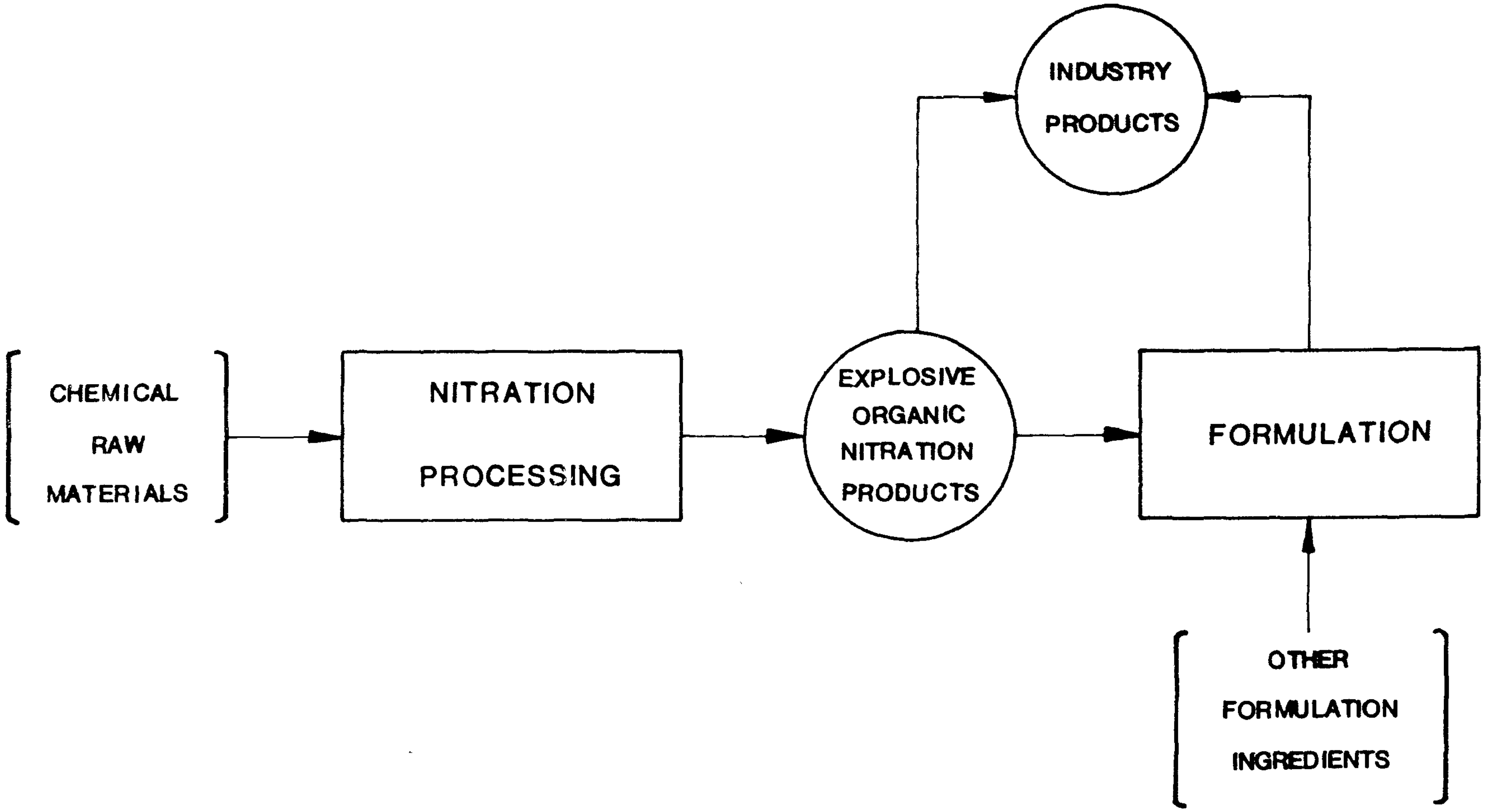

FIGURE 1. PROCESSES IN THE EXPLOSIVES INDUSTRY

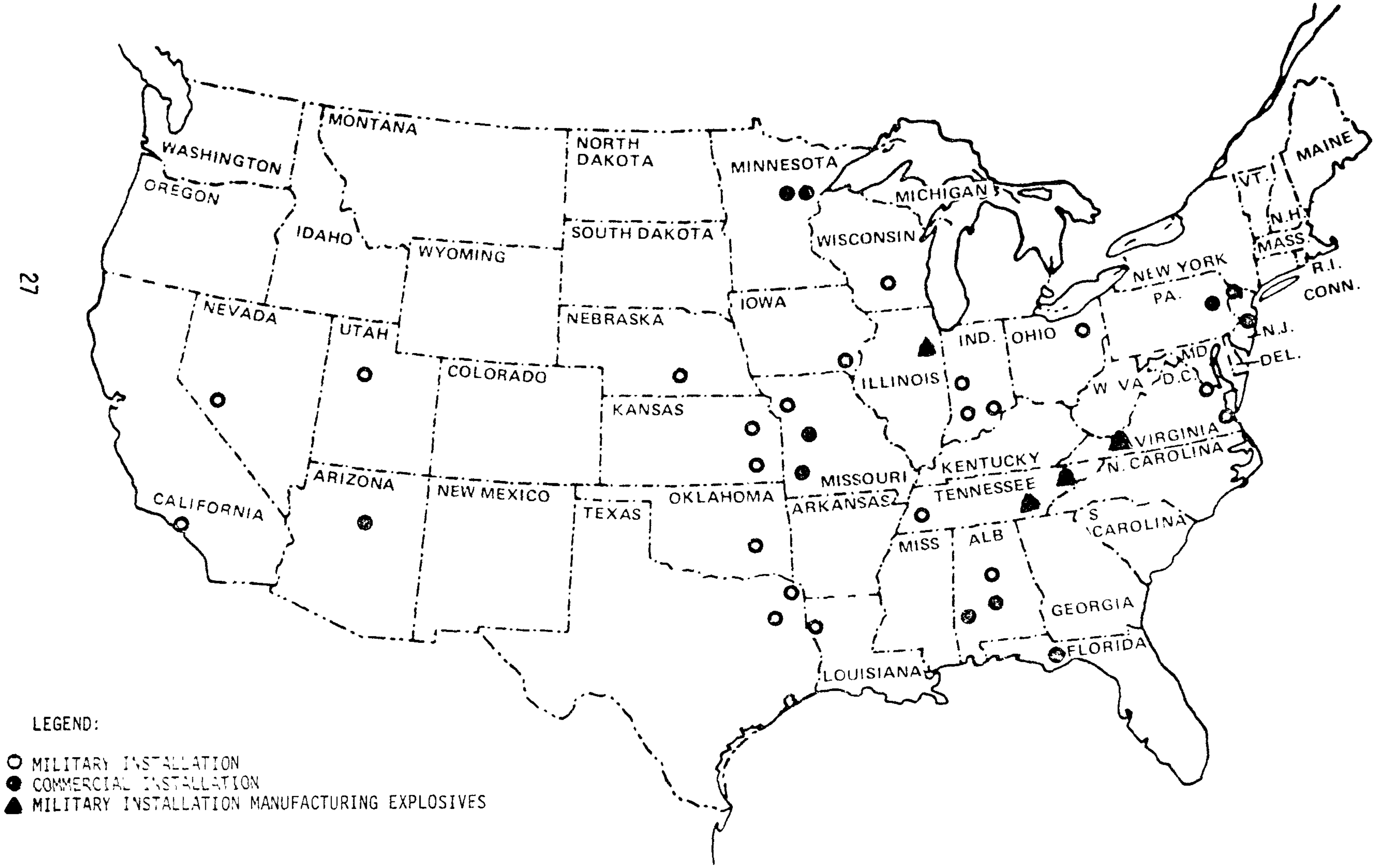

Figure 2 MAJOR EXPLOSIVES AND PROPELLANT FACILITIES IN THE U. S.

Source: Booz-Allen Applied Research, Inc. A Study of Hazardous Waste Materials. Hazardous Effects and Disposal Methods. 3 Vols. Vol. II, PB 221-466, Bethesda, Md., 1973.

Environmental Protection Agency. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Explosives Manufacturing Point Source Category. EPA 440/1-76/060-j, Group II, Washington, D.C., March 1976.

The commercial explosives industry had a 5.5 percent average annual growth rate in the 1969-1971 period. More recent quantitative data were not found. A study published in 1974 projected increased industrial demand for explosives based on an increased demand for coal as a domestic source of energy. The use of ammonium nitrate based explosives is predicted to increase relative to the use of other commercial products. Ammonium nitrate formulations have already replaced black powder and liquid oxygen, and it is predicted that the use of nitroglycerin based dynamites will also decline due to increased use of ammonium nitrate. Two commercial companies have discontinued production of nitroglycerin. Military explosives production rates are currently low and a number of plants are inactive and undergoing modernization. Mobilization of existing facilities would occur in the event of increased wartime demands for military explosives.

Some establishments within the industry produce electric power with on-site steam boilers and generators. Others produce process steam and purchase electricity. Table 1 presents a summary of fuels and electric energy consumed in 1971 by establishments in SIC Code 2892. It is not clear from the literature whether or not the consumption figures include the seven GOCO establishments classified in SIC Code 2892.

Table 1. FUELS AND ELECTRIC ENERGY CONSUMED IN 1971 BY COMPANIES IN SIC CODE 2892

Commodity	1971 Consumption
Coal	(547,000 s ton) 497 Gg
Distillate and residual fuel oil	(267,500 bbl) 42,500 m^3
Natural gas	(7 x 10^6 ft^3) 198 km^3
Purchased electric energy	630.3 GWh
Total energy used for heat and power	8.4 x TWh equiv

Source: U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census. 1972 Census of Manufacturers. Industry Series MC72(2)-28, Misc. Chemical Products, SIC Industry Group 289. December 1974.

Raw Materials

The general production process for the manufacture of explosives involves the nitration of an organic molecule peculiar to each explosive. Nitric acid is the nitrate source and, in most processes, sulfuric or acetic acid acts as a dehydrating agent. Typical of the organic molecules used are glycerin, toluene, cellulose, hexamine and pentaerythritol. After nitration, these molecules yield the following products: nitroglycerin (NG) and dinitroglycerin (DNG); trinitrotoluene (TNT) and dinitrotoluene (DNT); nitrocellulose (NC); cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX); and pentaerythritol tetranitrate (PETN), respectively.

As a general rule the parent organic compounds are imported to the manufacturing site. However, because of the large quantities of acids used in the production of explosives, most manufacturing plants maintain on-site acid production facilities. In general only the smaller plants, or those involved in specialty item production or R&D are known to import acids.

Nitric acid is made by oxidation of ammonia (AOP), with subsequent absorption of NO_2 in the reaction water. Nitric acid concentration procedures involve distillation of HNO_3 from sulfuric acid or magnesium nitrate solutions. Sulfuric acid is made by one or another version of the classic contact process wherein SO_2 is oxidized to SO_3 and absorbed in water (or previously made 100% H_2SO_4) to produce sulfuric acid (or oleum). In the conventional version of the process, SO_2 is a product of the combustion of sulfur in air. In the closely related sulfuric acid recovery (SAR) process, SO_2 is derived from the decomposition of spent H_2SO_4 in a cracking furnace. The SO_2 is oxidized to SO_3 by passage, in air, over a vanadium pentoxide catalyst.

Military explosives manufacturing plants engaged in the production of RDX/HMX purchase the acetic acid used but manufacture acetic anhydride on site. The anhydride is made from glacial acetic acid by thermal cracking of the acid to ketene gas and reaction of the ketene with more acetic acid to form acetic anhydride, which is then refined by simple distillation.

Most raw materials utilized in purification or refinement of the various explosive products, such as soda ash (Na_2CO_3), ammonium bicarbonate, acetone, and cyclohexanone are imported. A partial exception to this generality is sodium sulfite (Na_2SO_3), used in preparation of "sellite" for TNT purification. Most older TNT production facilities prepare sellite by the oxidation of sulfur. Sulfur dioxide (SO_2) gas so formed is scrubbed countercurrently with water to remove the trioxide and other impurities and then absorbed by a soda ash solution in a countercurrent packed tower. In the modernized, continuous TNT production process sellite is prepared directly from dry Na_2SO_3, which is imported.

Water may be considered an additional raw material. The bulk of water consumed during explosives manufacturing is utilized for cooling purposes. Nevertheless, a considerable volume of process water is consumed during the various purification procedures, with lesser volumes utilized during nitration steps, for reagent preparation, steam generation and cleanup.

Certain chemical substances such as lime ($CaCO_3$) and sodium hydroxide are used primarily for treatment of waste waters from the various production facilities. Specific data relating to the origin of such materials were not found in sources consulted for this study. However, it is reasonable to assume that they, like other incidental raw materials, are imported.

A quantification of the usage of pertinent raw materials, per unit of explosive produced, appears under the process description for specific explosives. Usage data for incidentals is generally not specified.

A list of raw materials for organic nitration processes as well as formulation (LAP) operation appears in Appendix A.

Products

Within the scope of this chapter, only those explosive compounds prepared by chemical conversion of organic feedstock to an organic nitrate have been examined. This group of compounds was further culled to eliminate materials prepared in limited quantities using "bench-top" methods and those materials prepared for experimental purposes.

Exclusion of explosive compounds other than organonitrates eliminates from this consideration the most important commercial high explosive. Ammonium nitrate-fuel oil (ANFO) mixtures, introduced as an explosive in the 1950's, accounted for nearly 80 percent of total commercial explosives usage in 1972. ANFO production is primarily a load, assembly, and pack (LAP) operation and, like other LAP operations, is outside the scope of this chapter. Manufacture of ammonium nitrate is described in Chapter 22.

Trinitrotoluene (TNT) is the most extensively produced military high explosive, with a production volume during 1969-1971 exceeding 20 Gg (22 thousand tons)/month. Unlike other basic explosive agents, TNT finds widespread use as a prime blasting agent. In addition TNT is blended with other basic explosives such as RDX, HMX or PETN to produce formulations exhibiting optimum handling, storage and/or performance characterisitics. Because of the relatively high production costs involved, commercial use of TNT is low and is generally limited to formulation with other explosives in the manufacture of boosters or explosive slurry.

Nitrocellulose (NC), with 1969-71 production levels reaching over 11.3 Gg (12.4 thousand tons)/month, is the second largest volume product from the military sector of the U.S. explosives industry. Though NC is one of the most potent basic explosives, it is rarely used for that purpose. Uncolloided NC, in the dry state, exhibits a sensitivity to impact of the same order as nitroglycerin, with a detonation velocity only slightly lower. NC is, however, the fundamental ingredient used in the production of all gun propellants and many rocket propellants.

The polymolecularity of NC is responsible for mechanical and physical characteristics which make it nearly ideal for this role. The fibrous nature of NC may be eliminated and energy output controlled by colloiding with high-energy or fuel-type plasticizers and incorporating a wide variety of solid or liquid additives. Additional control of ballistic performance may be exercised by manufacture of propellant grains in many shapes and sizes, from small flat sheets to large grains of intricate geometric pattern.

Cyclotrimethylenetrinitramine, or RDX, is the third most important munitions explosive with monthly production (1969-71) reaching as much as 6.8 Gg (7.5 thousand tons). Cyclotetramethylenetetranitramine, or HMX, a compound with explosive properties similar to those of RDX, is produced in much smaller amounts as by-product of RDX manufacture and is separated in the RDX purification process.

Both RDX and HMX are more powerful explosives than TNT, and they are considerably more sensitive in their refined state. When desensitized by addition of waxes, various oils or even with TNT, RDX/HMX formulations offer an excellent compromise of properties. RDX/HMX mixed with TNT finds widespread use as burster charges for artillery shells. Wax-desensitization makes RDX an excellent substitute for tetryl as booster charges in the fire train of various munitions. "Plastic" demolition explosives utilize RDX/HMX mixed with special plasticizers and solvents. HMX is used as a component of solid-fuel rocket propellants. Table 2 indicates production levels for the most extensively used RDX/HMX formulations. The production figures are estimated to represent 95 percent of total RDX output and 85 percent of total HMX output.

Nitroglycerin (NG) is used by the military primarily as an ingredient in double-base and triple-base propellants. In the commercial explosives industry NG may be used straight, for shooting oil wells, or as an ingredient in various dynamites and blasting gelatins. Many commercial manufacturers are beginning to phase out production of NG-based explosives primarily because other, less hazardous explosives perform as effectively for most commercial blasting operations. NG also finds limited use in the preparation of pharmaceuticals for treatment of cardiac conditions. During 1969-1971 military (GOCO) production of NG averaged 2.7 Gg/ (3000 tons).

During the years 1971 through 1973, annual commercial production for pentaerythritol tetranitrate (PETN) varied between 1.8 to 2.2 Gg (2.0 to 2.4 thousand tons). PETN exhibits properties characeristics of both initiators and detonating explosives. The brisance of PETN is greater than that of NG, while its sensitivity to impact and friction is less. It is classified as an initiating agent for handling and transportation purposes. Compression of the material increases the detonation velocity from 5.3 km/sec at only slight compression to 8.0 km/sec at a density of 1.62, and 8.3 km/sec at 1.70. PETN is used extensively in pressed form as core filler for Primacord, a detonating cord used for transmitting a detonation wave from one place to another without loss of time.

A combination of equal parts of TNT and PETN, called Pentolite, is widely used as a booster for initiating hard-to-detonate explosive slurries and prilled ANFO mixtures. PETN, like NG, is a vasodialator, and finds use in the preparation of pharmaceuticals used in treatment of cardiac conditions. Small doses have the effect of decreasing blood pressure while larger doses cause difficulty in breathing and convulsion.

Purification of PETN is a critical process in the production chain, since as little as 0.01% free acid or alkali in PETN markedly accelerates deterioration. Military specifications for this least stable of standard explosives limit acid/alkali content to 0.005%. Bulk quantities of dry PETN are highly susceptible to detonation, necessitating shipment and storage in a wet state (40% water).

A list of products from organic nitration processes as well as formulation (LAP) operations appears in Appendix B.

Table 2. PRODUCTION DATA (1972) FOR RDX/HMX EXPLOSIVE FORMULATIONS

Formulated Explosive	Components (% By Weight) RDX	HMX	TNT	Wax	Misc	Production (Gg)	Consumption (Gg) RDX	HMX	TNT
Composition A-3	91	---	---	9	----	1.093	0.993	---	---
Composition A-5	98.5	---	---	1.5	----	0.762	0.752	---	---
Composition B	60.5	---	38.7	0.8	----	68.991	41.739	---	26.698
Composition B-4	60.5	---	39.0	---	----	1.197	0.725	---	0.467
Composition C-4	91	---	---	---	9	1.115	1.016	---	---
Cyclotol	70	---	30	---	---	1.388	0.971	---	0.417
Octol	----	75	25	---	---	1.442	---	1.080	0.363
Totals						75.988	46.196	1.080	27.945

Source: American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

Companies

Explosives are manufactured by both privately owned commercial establishments and government owned, privately operated establishments. Both types of establishments manufacture organic nitration products including secondary high explosives, low explosives or propellants, and primary high explosives or initiators. Both types also produce formulated products in load, assemble and pack operations. The primary organic nitration products produced by commercial establishments are nitroglycerin and some nitrocellulose. Commercial establishments also produce numerous formulated products including dynamite and ammonium nitrate blends. Organic nitration products produced by military establishments include TNT, RDX/HMX, NG, and NC.

Table 3 summarizes operations conducted at military facilities. The Army conducts all large-scale explosives manufacturing. Seven of the military facilities are operated by private companies, as detailed in Table C-1 in Appendix C. Only three of these facilities are currently active. Table C-1 describes location, employment, sales, products, plant area, facilities, and production status for each of the seven GOCO plants.

Table 4 lists commercial establishments that manufacture organic nitration products. The companies in Table 4 either are listed in the 1976 Directory of Chemical Producers or were identified in an industry survey from questionnaires, telephone contacts, and information supplied from a file of data on U.S. industrial establishments compiled by Economic Information Systems, Inc. (EIS). Tables C-2 and C-3 in Appendix C give information on commercial establishments. Table C-2 lists companies from the 1976 Directory of Chemical Producers. Table C-3 gives more detailed information on commercial establishments which manufacture organic nitration products, compiled from an EIS survey. Data in table C-3 are based on direct company contact, the Census of Manufacturers, and statistics compiled by local authorities. Data in Tables C-2 and C-3 are inconsistent in some respects.

Table 5 lists major commercial producers of formulated explosives. Table 6 shows the number and location of explosives handling establishments licensed by the Bureau of Alcohol, Tobacco and Firearms of the Department of the Treasury. These establishments include facilities which use and distribute explosives as well as those which manufacture organic nitration products and prepare formulations. Table C-4 in Appendix C gives individual company data on explosives formulators.

Environmental Impact

Of the three categories of waste (liquid, gaseous, and solid) generated by the explosives industry, liquid wastes contain the most varied assortment of significant pollutants or potential pollutants. Components of the gaseous waste stream are more limited but are no less significant. Solid waste products are more limited still, and are generally minor contributors to environmental pollution problems.

Table 3. OPERATIONS AT MAJOR AMMUNITION PLANTS

Plant	Explosive Manufacture	Propellant Manufacture	Initiator Manufacture	Load, Assemble and Pack
ARMY				
Holston AAP	+			
Radford AAP	+	+		+
Joliet AAP	+		+	+
Badger AAP	+	+		
Lake City AAP		+	+	+
Longhorn AAP				+
Newport AAP	+			
Volunteer AAP	+			
Indiana AAP		+		
Iowa AAP				+
Kansas AAP				+
Louisiana AAP				+
Lone Star AAP				+
Milan AAP				+
Twin Cities AAP			+	+
Sunflower AAP		+		+
Cornhusker AAP				+
NAVY				
NOS Indian Head		+	+	+
NAD Yorktown				+
NAD Crane			+	+
NAD McAlester				+
NAD Hawthorne				+
Navy Magna Plant				+
AIR FORCE				
AF Plant 78				+

Sources: American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

Environmental Protection Agency. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Explosives Manufacturing Point Source Category. EPA 440/1-76/060-j, Group II. Washington, D.C., March 1976.

Table 4. COMMERCIAL PRODUCERS OF EXPLOSIVE ORGANIC NITRATION PRODUCTS

Air Products and Chemicals, Inc.
Apache Powder Co., Inc.
Atlas Chemical Industries (ICI United States, Inc.)
Austin Powder Co.
Bofors America, Inc.
E. I. duPont de Nemours Co.
Hercules, Inc.
Hummel Chemical Co., Inc.
Olin Corp.
Rubicon Chemicals, Inc.
Trojan - U. S. Powder (Commercial Solvents Corp.)

Table 5. MAJOR COMMERCIAL PRODUCERS OF FORMULATED EXPLOSIVES

Company	Estimated 1974 Sales (Million$)[2]
[1]American Cyanamid Company	
[1]Apache Powder Company	9.0
[1]Atlas Explosives Division, ICI United States Incorporated	2.4
[1]Austin Powder Company	24.4
Dow Chemical Company	0.9
[1]E. I. du Pont de Nemours & Company, Inc.	49.0
Ensign-Bickford Company	3.0
Explosives Corporation of America	
General Aluminum Smelting Company	
Gulf Energy and Environmental Systems	
Gulf Explosives	
Harrison Jet Guns, Inc.	0.9
Hawkeye Chemical Company	
[1]Hercules Incorporated	52.6
Ireco Chemicals	3.9
Jet Research Center	4.5
Logan Corporation	
McCormick Selph (Teledyne)	7.5
Mesabi Blasting Agents	0.9
Monsanto Company	0.6
Nobel's Explosives Company Ltd.	
Olin Energy Systems	15.0
Phillips Petroleum (Blasting Materials Division)	
Titan Explosives Co.	1.5
[1]Trojan - U.S. Powder Division of Commercial Solvents Corporation	
U.S. Steel Corporation	
West Virginia Belt Sales and Repairs Incorporated	

[1]These companies also produce explosive organic nitration products.
[2]Sales estimates taken from data in Tables C-3 and C-4 in Appendix C.

Table 6. NUMBER OF EXPLOSIVES HANDLING PLANTS

By U. S. EPA Regions

EPA Region	Commercial Plants	Military Plants Active	Military Plants Inactive	Combined Total
1	18	0	0	18
2	24	1	1	26
3	108	2	3	113
4	78	3	1	82
5	103	4	3	110
6	69	7	0	76
7	43	3	4	50
8	46	0	1	47
9	76	1	1	78
10	21	0	0	21
TOTALS	586	21	14	621

Source: Environmental Protection Agency, Effluent Guidelines Division. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Explosives Manufacturing Point Source Category. EPA 440/1-76-060-j, Group II. Washington, D. C., March 1976.

Liquid waste streams from the explosives industry vary according to production processes and products. As stated in the industry description, four categories have been established to describe the various operations of the industry: explosives manufacture, propellant manufacture, LAP operations, and initiator manufacture. Seven parameters of raw waste loading are considered significant to the establishment of waste-water effluent limitations and guidelines: biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), total suspended solids (TSS), nitrate-nitrogen (NO_3-N), total Kjeldahl nitrogen (TKN) and sulfate (SO_4).

Table 7 presents average raw waste load data in terms of the above parameters for each of the four categories. The wide variability in loading is due in part to the nature of the products. Other contributing factors include product demand (wartime vs. peacetime requirements) as well as data availability and military/commercial data combination.

Certain of these parameters are influenced chiefly by specific raw materials used in the process. The BOD, COD and TOC can be attributed to the organics involved in nitration or subsequent finishing operations. Nitrogen levels (NO_3-N and TKN) result primarily from nitric acid and organonitrates (product as well as by-products). Sulfate levels can be attributed to sulfuric acid and, in the case of TNT production, to the sellite used in purification.

As previously stated, the manufacture of explosives involves the nitration of organic compounds followed by product finishing including washing, refinement and drying or dewatering. The various finishing operations are the major contributors to the waste-water streams. Process waters from nitration and certain finishing operations are highly acidic, but in most cases these wastes are neutralized with an excess of lime prior to discharge. Such neutralization has the effect not only of creating an alkaline waste stream but also of elevating the dissolved solids content of the waste water.

Discharge of explosive compounds in the waste water is a potential problem. Sources indicate that explosives concentrations as high as 1000 mg/ℓ for NG have been recorded. Waste water containing 100 mg/ℓ TNT is typical, while RDX/HNX concentrations can be as high as 25 mg/ℓ. The presence of TNT in waste water is of special concern, since it has been proven to inhibit natural biological processes.

Contamination of the waste water streams with explosive material can, in some cases, lead to contamination of the soil immediately surrounding the stream. The soil may then become a source of continued contamination, even after termination of manufacturing operations. A history of this type of pollution exists within the industry, encountered during the manufacture of tetryl.

All military production of tetryl was confined to Joliet Army Ammunition Plant (JAAP) for a number of years. Because of a similarity in sensitivity and explosive properties between tetryl and RDX, the explosive and toxic hazards involved with handling dry tetryl, and certain economic considerations involved, the Army phased out tetryl production. Manufacturing operations ceased as of 31 July 1973. While tetryl was in production, waste water containing the explosive was discharged to drainage ditches. At one point

Table 7. **EXPLOSIVES MANUFACTURING RAW WASTE LOADS IN WEIGHT PER UNIT WEIGHT OF PRODUCTION**

Category	Products	Flow/Production	Raw Waste Loads (kg/Mg Product)[a]						
		m^3/Mg	BOD	COD	TKN	Nitrates	Sulfates	TOC	TSS
A. Manufacture of Explosives	Dynamites, NG, NH_4NO_3, TNT, RDX, HNX	1.68	1.46	3.87	.82	2.50	6.90	1.63	0.82
B. Manufacture of Propellants	NC, Single, Double, Triple Base Propellants, High Energy Propellants Rolled Powders	267	63.4	118	5.98	38.4	191	43.6	64.5
C. Load Assemble and Pack Plants	Primers, Fuses, Shells Blasting Caps, NCN, Water gels, slurries, ANFO	1.76	0.0005	0.08	0.021	0.015	0.409	0.004	0.92
D. Manufacture of Initiators	Manufacture of Initiators such as Primer Explosives, Lead Azide, HNM, LMR, PETN, Lead Styphinate, Mercury Fulminate	873	1170	6290	3.00	5.50	927	851	49.3

[a]Equivalent to lb/1000 lbs Product

Source: Environmental Protection Agency, Effluent Guidelines Division. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Explosives Manufacturing Point Source Category. EPA 440/1-76-060-j, Group II. Washington, D.C., March 1976.

in 1969 one observer reported tetryl crystals visible in the drainage ditches. On 14 August 1973, 45 days after production ceased, water and soil samples were taken at points downstream from the point of outfall of tetryl waste water. Assay data from these samples are presented in Table 8. It is estimated that the soil at JAAP contains 14,000 kg of tetryl. At a constant depletion rate of 2000 kg/year, elimination of tetryl from the soil would take seven years. With a regressive rate of depletion, total leaching would take longer.

Process descriptions for tetryl production are not included in this report because the material is no longer in production and is not expected to be produced in significant quantities in the future. The emissions history associated with tetryl production is presented as an indication of certain long-range pollution problems which may be encountered within the industry.

The waste loads associated with propellant manufacture are generally higher than those associated with explosive manufacture (see Table 7).

Because of the variety of raw materials involved in formulation of propellant powders, qualitative differences are also seen in the waste generated by operations in the two categories. High TSS values are typical of these operations, specifically during manufacture of nitrocellulose. One source indicates that over 4000 kg of nitrocellulose fines were lost daily during peak production at Radford Army Ammunition plant. High BOD, COD and TOC levels can be attributed to organics and solvents used in processing. Nitrogen levels can be attributed to nitric acid and organonitrates while sulfate loading can be related to the use of sulfuric acid. Sources indicate an almost total lack of significant waste water treatment during propellant manufacturing operations. Generally, treatment consisted of acid neutralization and in some cases sedimentation.

Load, assemble and pack (LAP) operations exhibited the lowest waste loading for the seven parameters shown in Table 7. This is consistent with the nature of such operations. However, waste waters from LAP generally show relatively high contamination by the explosive compounds being processed. Table 9 presents data for such contamination from selected military plants engaged in LAP operations.

Waterborne waste loads associated with the manufacture of initiating compounds are the highest of any explosives manufacturing operation. This high waste loading results from circumstances unique to this category of the explosives industry. Since initiating compounds are used to detonate other explosive agents, the relative need for this class of material is small. Because of limited requirements, batch production methods are usually employed. For economic reasons, recovery of spent materials on such a small scale is not considered feasible and waste water treatment facilities are nonexistent. Average raw waste loads from initiator manufacture are shown in Table 9. It is clear from an examination of the table that, with the limited flow rates common to this segment, small changes in absolute raw waste discharge would create extreme changes in waste loading. The nature of operations in this category bears out the variability of raw waste loading of effluent waters. With the limited production requirements common to initiating compounds, waste streams show high pollutant concentration during production followed by long periods of low pollutant concentration during process inactivity.

Table 8. ASSAY OF WATER AND SOIL SAMPLES FROM TETRYL REFINERY DITCH JOLIET ARMY AMMUNITION PLANT, 14 AUGUST 1973

Sample	Description	Tetryl Content mg/ℓ Liquid or mg/10 g Soil
1	Standing water in ditch	0
2	Surface soil approximately 15 cm from edge of flow	4.72
3	Seepage water from 10 cm deep hole dug at site of sample 2	44
4	Sub-surface soil from hole dug at site of sample 3	844
5	Surface soil approximately 60 cm from edge of flow	5.62
6	Sub-surface soil, 10 cm deep from site of sample 5	14.5

Source: The American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D. C., Oct. 1975.

Table 9. **WASTE WATERS GENERATED IN LAP OPERATIONS**

AAP[a]	Activities	Raw Materials	Flow m^3/day	Pollutants	Discharge Load kg/day	Comments
CAAP	Load 8-inch shells	TNT	75.7[b]	57 mg/l TNT	~4.3(TNT)	Disposal in evaporation ponds
	Load 500-, 750-, and 1,000-pound bombs	Tritonal (80% TNT and 20% flaked Al)				
	Laundry		54.8	2.7 mg/l TNT	~0.13(TNT)	Disposal in dry streams
	Overall		131		4.4(TNT)	
IAAP	Shell loading		341 (94.6)	Pink water 1 mg/l TNT[d] 145 mg/l RDX[c] 20 mg/l RDX[d]	0.34(TNT)[d] 49.4(RDX)[c] 6.8(RDX)[d]	Wastes subjected to diatomaceous earth filtration followed by adsorption on granular carbon columns
	Laundry		30.3	10 mg/l TNT	0.31(TNT)[c]	Discharged to surface streams
	Mold booster charges from bulk explosives		0.814	Tetryl		
	Overall		371		0.64(TNT) 49.4(RDX)[c] 6.8(RDX)[d]	

(Continued)

Table 9. (Continued) WASTE WATERS GENERATED IN LAP OPERATIONS

AAP	Activities	Raw Materials	Flow m^3/day	Pollutants	Discharge Load kg/day	Comments
InAAP	Fabricate cloth bags and paper tubes and load propellants into these containers for shipment	N.A.	N.A.	N.A.	N.A.	
JAAP	Loading of medium caliber ammunition and ammunition components	Composition-B being loaded into 105 mm shells at a rate of 200,000 shells per month	23.5	TNT 145 mg/l RDX[c] 20 mg/l RDX[d]	3.4(RDX)[c] 0.45(RDX)[d]	Filtered through diatomaceous earth and then through two granulated charcoal
KAAP	Load explosives, primarily formulations of TNT and RDX, into ordnance items	TNT, RDX	N.A.	TNT, RDX	N.A.	Currently wastewaters are disposed of by trucking them to evaporative ponds
	Detonators for 105 mm howitzer shells	Lead azide, lead styphnate, RDX	N.A.	N.A.		$NaNO_3$, acetic acid, and NaOH used to deactivate the lead azide

(Continued)

Table 9. (Continued) WASTE WATERS GENERATED IN LAP OPERATIONS

AAP	Activities	Raw Materials	Flow m^3/day	Pollutants	Discharge Load kg/day	Comments
LSAAP	Melt-pour (Area O)	Composition-B	N.A.	Pink water NO_3,TOC,color, TNT,pH	N.A.	Discharged to lagoon system
	Melt-pour (Area C)	Composition-B				
	Melt-pour (Area E)	TNT and Composition-B	75.7[e]	Pink water NO_3,TOC,color, TNT,pH	N.A.	Recycled
	Melt-pour (Area G)	Octyl,TNT, and Composition-B				
	Load Line (Area P)	Lead azide	N.A.	N.A.	N.A.	Batch destruction by use of ceric ammonium nitrate
	Load Line (Area Q)	Lead azide	N.A.	N.A.	N.A.	
	Black-powder load	Black powder	None except raw sewage and storm-water runoff	N.A.	N.A.	Spilled powder is dumped into surface waters
LHAAP	Mixing, processing	N.A.	N.A.	BOD,COD,Mn, Cn-,NO_3,PO_4, Fe,Cd,poly-sulfide polymers, aluminum powder, black powder, and ammonium perchlorate	N.A.	Ammonium perchlorate goes to surface water. All solids go to evaporative ponds and are eventually incinerated. Remaining wastes go to surface water

(Continued)

Table 9. (Continued) WASTE WATERS GENERATED IN LAP OPERATIONS

AAP	Activities	Raw Materials	Flow m^3/day	Pollutants	Discharge Load kg/day	Comments
LAAP	Shell-loading	N.A.	522	80 mg/l TNT	41.7	Waste is trucked to leaching ponds on the plant grounds
MAAP	N.A.	N.A.	1,510	.5 mg/l RDX 1.0 mg/l TNT	0.90(RDX) 1.36(TNT)	Wastewaters are discharged to a drainage canal which flows to surface water
	Shell washout	N.A.	2.10	145 mg/l RDX[2] 40 mg/l TNT[2]	0.31(RDX) 0.239(TNT)	
	Overall	N.A.	1,510		1.22(RDX) 1.58(TNT)	
RaAAP	N.A.	N.A.	N.A.	N.A.	N.A.	

[a]Acronyms used to identify Army Ammunition Plants (AAP):

CAAP	Cornhusker	LHAAP	Long Horn
IAAP	Iowa	LSAAP	Lone Star
InAAP	Indiana	MAAP	Milan
JAAP	Joliet	RaAAP	Ravenna
KAAP	Kansas	VAAP	Volunteer
LAAP	Louisiana		

[b]Primarily washdown waters
[c]Before treatment
[d]After treatment
[e]Includes raw sewage and storm-water runoff

N.A. = Data not available

Source: The American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D. C., Oct. 1975.

Contamination of waste water with heavy metals, i.e., lead and mercury, appeared significant only in Category D, Manufacture of Initiators. Mercury from fulminate production and lead from the production of lead azide and lead styphnate are found in process effluents. One source indicates a daily discharge of approximately 1 kg lead (200 mg/ℓ Pb concentration in waste stream) from one such production facility. This source also states, however, that information available on heavy metals contamination was not adequate to establish guidelines for effluent limitations.

The major sources of gaseous emissions from explosives manufacturing are processes involving the manufacture, concentration and recovery of acids used in the nitration process. Oxides of nitrogen (NO_x) and sulfur (SO_x) are characteristic of the emissions from these processes. Acid mists also appear as emissions from nitration processes. A summary of gaseous emissions characteristic of organic nitration process is presented in Table 10. Measures for control or abatement of NO_x or SO_x in such emissions have been virtually nonexistent in the industry. Absorption towers for exhaust gas scrubbing have found limited application, mainly during acid concentration processes. Several commercially available control systems are currently being tested at military production facilities, including molecular sieve devices and oxide reduction systems. An extended absorption method, based on passage of exhaust gases through two scrubber systems, is also being tested.

The various nitration processes show more limited NO_x and SO_x emissions. In the case of TNT manufacture, toluene may be found as a component of the gaseous waste stream. Trinitromethane (TNM), a violent explosive, is a gaseous by-product of the nitration process and may also be found in emissions from nitration reactors. Current practice is to discharge TNM to the atmosphere. Some TNM is found, however, in acid and fume recovery systems, creating a potentially hazardous situation.

Organics used in the various finishing processes and in propellant formulation contribute some loading to the gaseous waste streams from these operations. Gaseous hydrocarbon emissions result primarily from fugitive vapors from various solvent recovery operations.

Current practice for disposal of selected solid wastes contributes also to the generation of atmospheric pollutants. Explosives contaminated packaging material as well as most explosive wastes not suitable for reclamation are disposed of by open burning. Contaminated NG is generally purposely detonated rather than reclaimed because of its extreme sensitivity and unpredictability. Such disposal methods result in uncontrolled emission of gaseous waste (primarily NO_x) and particulate matter.

The balance of solid wastes generated during manufacturing operations, such as sulfate residue from sellite incineration and various sludges from settling lagoons is disposed of by surface dumping or in sanitary landfill operations. Depending on ambient conditions, leaching of soluble materials from disposal sites may contribute to waste loading of surface or ground waters and may result in long-term pollution problems.

Table 10. SUMMARY OF GASEOUS EMISSIONS FROM ORGANIC NITRATION FACILITIES

Source	SO_x		H_2SO_4 Mist		NO_x		HNO_3 Mist	
	g/kg	ppm	g/kg	ppm	g/kg	ppm	g/kg	ppm
TNT MFG (Acid Fume Recovery System)								
Uncontrolled								
Average	-	-	-	-	45	20,700	-	-
Range	-	-	-	-	27.6 - 80	2,640 - 64,600	-	-
Controlled								
Average	-	-	-	-	10.5	288	-	-
Range	-	-	-	-	9.3 - 11.3	235 - 341	-	-
NITROGLYCERIN MFG								
Uncontrolled								
Average	-	-	-	-	46.5[1]	23,000[1]	-	-
Range	-	-	-	-	-	N/A	-	-
NITROCELLULOSE MFG								
Uncontrolled								
Average	0.38	22.3	-	-	21	768	-	54.5
Range	0.23 - 0.54	nil - 160	-	-	16.6 - 22.9	170 - 1,860	-	nil - 3,080
Controlled								
Average	-	-	-	-	38	390	-	-
Range	-	-	-	-	1.9 - 6.0	130 - 550	-	-
RDX (HMX) MFG								
Uncontrolled								
Average	-	-	-	-	6.9[1,2]	high	-	-
Range	-	.	-	-	N/A	N/A	-	-

(Continued)

Table 10. (Continued) SUMMARY OF GASEOUS EMISSIONS FROM ORGANIC NITRATION FACILITIES

Source	SO_x		H_2SO_4 Mist		NO_x		HNO_3 Mist	
	g/kg	ppm	g/kg	ppm	g/kg	ppm	g/kg	ppm
AMMONIA OXIDATION PLANT								
Uncontrolled								
Average	-	-	-	-	7.0	2.430	-	-
Range	-	-	-	-	2.4 - 18.5	1,400 - 5,700	-	-
Controlled								
Average	-	-	-	-	1.05	11.7	-	-
Range	-	-	-	-	0.13 - 1.8	nil - 61.8	-	-
NITRIC ACID CONCENTRATION								
Uncontrolled								
Average	-	-	-	-	4.4	21,700	0.19	350
Range	-	-	-	-	0.5 - 16.7	7,700 - 39,600	0.016 - 0.5	107 - 490
SPENT ACID RECOVERY								
Uncontrolled								
Average	-	-	-	-	0.80	3,010[3]	0.006	22[3]
Range	-	-	-	-	0.23 - 1.1	1.090 - 4,030	0.003 - 0.009	11 - 41
H_2SO_4 REGENERATION AND CONCENTRATION								
-H_2SO_4 Regenerator								
Uncontrolled								
Average	6.8	251	0.79	44	1.2	352	-	-
Range	0.9 - 28.5	163 - 350	nil - 2.6	30 - 55	0.42 - 2.35	285 - 410	-	-
-H_2SO_4 Concentrator								
Uncontrolled								
Average	1.9	170	2.05[1]	N/A	1.2[1]	170	-	-
Range	0.64 - 2.6	62 - 320	N/A	1.2 - 1,440[4]	N/A	110 - 320	-	-

(Continued)

Table 10. (Continued) SUMMARY OF GASEOUS EMISSIONS FROM ORGANIC NITRATION FACILITIES

Source	SO_x g/kg	SO_x ppm	H_2SO_4 Mist g/kg	H_2SO_4 Mist ppm	NO_x g/kg	NO_x ppm	HNO_3 Mist g/kg	HNO_3 Mist ppm
H_2SO_4 REGENERATION AND CONCENTRATION (Continued)								
-Oleum Plant								
Uncontrolled								
Average	19.7	2,880	0.55	90	-	-	-	-
Range	6.3 - 32	700 - 6,670	0.43 - 0.80	4 - 280	-	-	-	-

1. Only one data point available.

2. HMX is assumed to have the same emission rate as RDX.

3. Only one data source found.

4. The wide range is due to data taken at Sunflower AAP which had a significant H_2SO_4 misting problem.

Source: Nelson, T. P. and R. E. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319, Task 50, July 1976.

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INDUSTRY ANALYSIS

Organic nitration processes leading to the production of explosive compounds are described in this chapter. Five nitration processes are described along with the process for manufacture, concentration and recovery of nitric acid used in the nitration reactions. In several cases, process descriptions are somewhat generalized in order to encompass minor operational variations between batch and continuous flow production techniques.

Each operation is represented by a flow chart indicating input materials (brackets), processes (numbered rectangles), and product or by-product streams (large circles). Solid, liquid, and gaseous waste streams are indicated by small squares, triangles and circles, respectively, attached to the numbered process rectangles. Process descriptions follow the flow charts on which they are presented.

Data are given in metric units according to the System Internationale described in the ASTM Metric Practice Guide. Preferred base units and rules for rounding numbers converted from one system of units to another are described therein.

The information used to prepare this catalog entry consisted of books, encyclopedias, results of EPA supported investigations, replies to questionnaires submitted to representatives of commercial and governmental production facilities and results of field surveys at selected production installations. Additional sources of information exist, such as patent literature and publications of Stanford Research Institute's Process Economics Program, which were not utilized because of the limited resources available for this study. The reader is advised to consult such additional sources of information on subjects which were not treated in sufficient depth to meet specific needs.

There are some recognized deficiencies and inconsistencies in the data used to prepare this report. Many commercial facilities consider data relating to raw materials consumption or production as proprietary information. Certain governmental (GOCO) production facilities for which information was gathered and used in the preparation of this study have since reduced production, eliminated certain products from their line, or ceased operations altogether. Others are in the process of modernizing operations, or are actively engaged in development of pollution abatement programs which were only in planning stages when source information for this study was generated. Inconsistencies appear also in lists of commercial producers of organic nitration products. Producer/product data compiled from the 1976 Directory of Chemical Producers differ somewhat from such data compiled by a telephone survey of producers listed in an EIS data file. Limited attempts to resolve this inconsistency were unsuccessful and the data are presented as compiled.

Nitric Acid Production Processes

Production of nitrating acids is the largest operation in the explosive manufacturing system. All military explosives manufacturing plants and most of the major commercial plants make their own acid. At recent production rates (1969-1971) the volume of H_2SO_4 manufactured by military explosive plants was four times the volume of TNT produced and 4 percent of the U.S. total for all purposes. Nitric acid and oleum production levels were correspondingly high (see Figure 3).

The various nitration processes use nitric acid either alone or in conjunction with sulfuric acid (oleum) or acetic acid to produce the desired product. Spent acids from nitration are processed to recover unused HNO_3 as well as H_2SO_4 or acetic acid. The recovered acids are then either recycled or disposed of as by-products.

Within the scope of this study only those processes involving the production and recovery of nitric acid are examined. Figure 4 is a flow chart for the processes described.

The high-pressure ammonium oxidation process described in Process No. 1 is typical of current production methods. The National Emission Data System shows a Source Classification Code and emission factor for older, low-pressure process, but sources consulted for this study failed to identify any manufacturing facility still producing HNO_3 by the older method.

Process Nos. 2 and 3 are typical of nitric acid concentration (NAC) and spent acid recovery (SAR) operations in general. However, for purposes of establishing Source Classification Codes and emission factors, the National Emission Data System treats nitric acid concentration (NAC) from TNT spent acid recovery (SAR) separately from NAC during original production of nitric acid. In a like manner H_2SO_4 regeneration during TNT-SAR is assigned a unique SCC and specific emission factors. For the purposes of this study, NAC and SAR are considered to be processes common to a number of process groups.

Acid production and recovery plants are major contributors to the waste stream entering the atmosphere from the explosives industry. Emissions from absorber stacks routinely appear as visible plumes, indicating high NO_x or SO_x concentration in the tail gas stream.

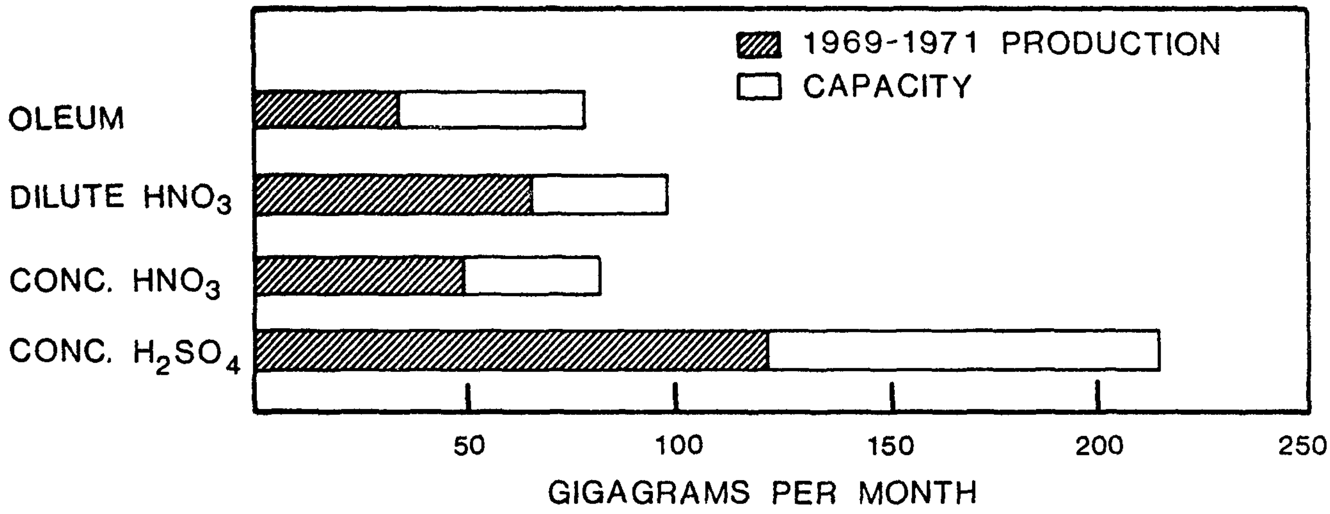


FIGURE 3. PRODUCTION OF NITRATION ACIDS

Source: American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

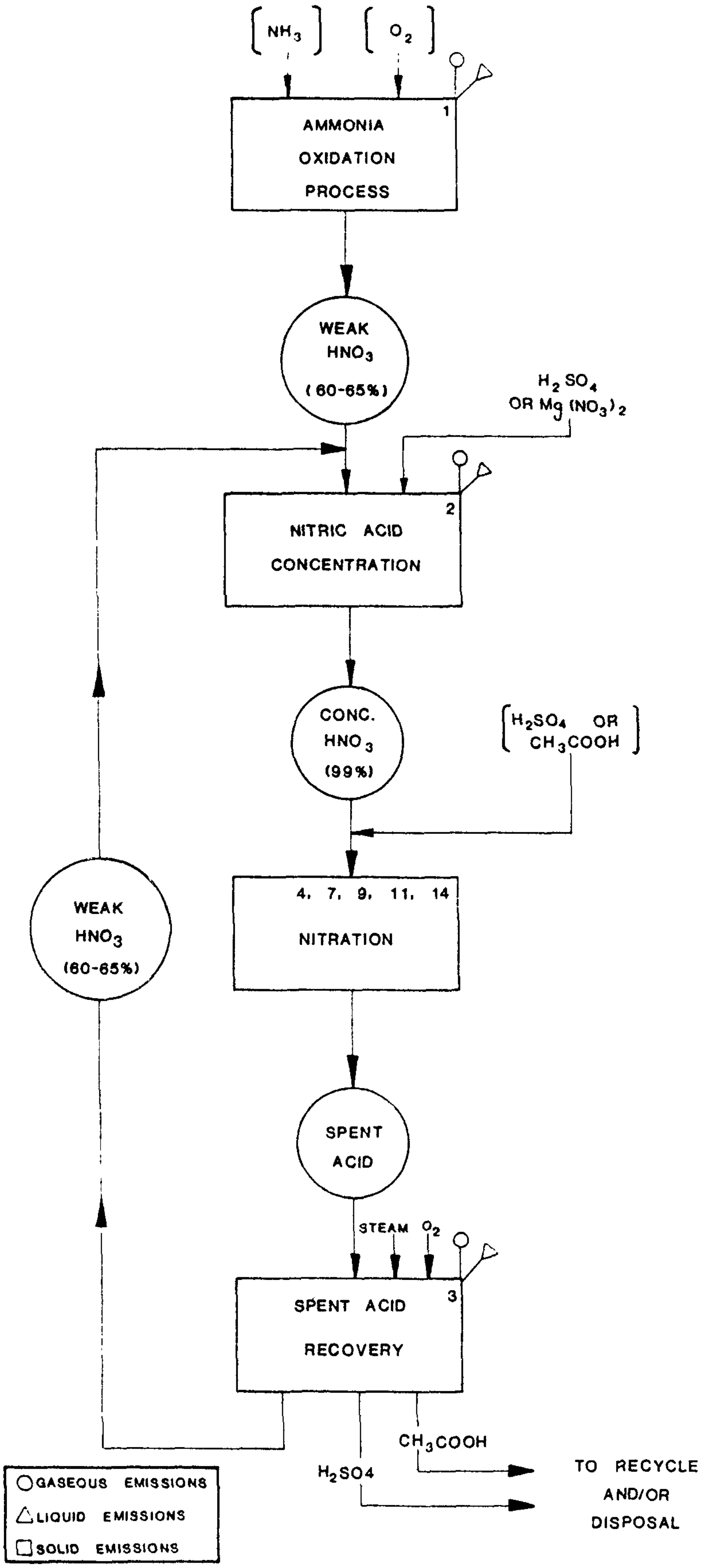


FIGURE 4. FLOW CHART FOR NITRIC ACID PRODUCTION

Ammonia Oxidation Process (AOP)

1. Function - Anhydrous ammonia is vaporized, mixed with preheated air and combusted under pressure in the presence of a catalyst to produce nitric oxide (NO) which is further oxidized by the excess air to nitrogen dioxide (NO_2) and its dimer (N_2O_4). The equilibrium mixture is absorbed in water in a cooled absorber tower to form weak (60-65%) HNO_3. The NO formed at the same time is reoxidized to form additional HNO_3. These chemical reactions are represented by the following equations.

$$12\ NH_3 + 15\ O_2 \longrightarrow 12\ NO + 18\ H_2O \qquad (1\text{-}1)$$

$$12\ NO + 6\ O_2 \longrightarrow 12\ NO_2 \qquad (1\text{-}2)$$

$$12\ NO_2 + 4\ H_2O \longrightarrow 8\ HNO_3 + 4\ NO \qquad (1\text{-}3)$$

2. Input Materials - Anhydrous ammonia gas and preheated air constitute the feed stream to the catalytic oxidizer. Ammonia consumption is approximately 0.4 kg/kg HNO_3 produced. Conversion is at least 95 percent of theoretical.

3. Operating Parameters - The ammonia/air mixture passes through a catalyst bed at a temperature of 800 to 960°C and a pressure of 929 kPa (120 psig). The reaction air is first compressed and preheated to 260°C by hot reaction gasses from the catalyst bed. Sources consulted indicate platinum-rhubidium as well as platinum-palladium-mercury may be used to catalyze the reaction.

4. Utilities - Specific data relating to utilities consumption were not found in the sources consulted for this study. However, one source indicates effective utilization of heat generated during catalytic oxidation by passing the reaction gases through heat exchangers to: 1) preheat reaction air, 2) reheat tail gases, 3) produce steam for the compressor turbine and 4) produce steam for export from the process.

5. Waste Streams - The only source for atmospheric emissions from the AOP is tail gas from the absorption tower. The National Emission Data System listing shows emission factors of 26.25 g NO_x/kg HNO_3 for the older (atmospheric pressure reaction) oxidation process and 2.5 g NO_x/kg HNO_3 for the newer (high pressure) process described here.

A summary of gaseous emissions from AOP at two commercial facilities and six Army ammunition plants is presented in Table 11. Only three of the AAP's are currently in operation.

Waste waters from AOP facilities include cooling water and leakage, as well as water used for cleanup. Because AOP effluents are normally mixed with large volumes of cooling water and are frequently combined with wastes from NAC and sulfuric acid processes, it is difficult to specify pollutant discharges solely associated with AOP. A study of AOP at one military production facility, Holston Army Ammunition Plant (HAAP), resulted in waste-water data summarized in Table 12. From this it may be seen that, beyond the expected highly acidic

Table 11. GASEOUS EMISSIONS FROM AMMONIA OXIDATION PLANT PROCESSES

Source	Source Location	Exit Gas Flow Rate m^3/s	Emission Unit	kg/unit HNO_3	kg/unit NO_x	Annual Prod. Gg
Ammonia Oxidation	Holston AAP	N/A	Mg-Nitric Acid (61%)	-	-	0[a]
Weak HNO_3 Prod.[b]	Volunteer AAP	Unk	Mg-Weak HNO_3	-	1.38	5.77
Strong HNO_3 Prod.[c]	Volunteer AAP	Unk	Mg-Strong HNO_3	-	3.77	4.49
Ammonia Oxidation	Sunflower AAP	N/A	Mg-HNO_3 (60%)	-	18.5	16.6[d]
Ammonia Oxidation	Sunflower AAP	N/A	Mg-HNO_3 (62%)	-	1.65	99.3
Ammonia Oxidation	Hercules Bessemer, Al.	0.317 @ 716 kPa (88 psig) 26.6°C	Mg-HNO_3 (100%)	uncontrolled controlled	18.3 0.12	18.2
Ammonia Oxidation	Apache Chemical Benson, Arizona	-	Mg-HNO_3 (100%)	-	1.75[e]	-
Ammonia Oxidation	Badger AAP	1.47	Mg-HNO_3 (62%)	-	3.75	53.6[d]
Ammonia Oxidation	Badger AAP	1.68	Mg-HNO_3 (62%)	-	4.65	56.9[d]
Ammonia Oxidation	Badger AAP	1.55	Mg-HNO_3 (62%)	-	2.40	62.2[d]
Ammonia Oxidation	Sunflower AAP	1.89	Mg-HNO_3 (100%)	-	8.05	24.2
Ammonia Oxidation	Holston AAP	2.22	Mg-HNO_3 (100%)	-	12.9[f]	18.2
Ammonia Oxidation	Holston AAP	2.22	--	-	0.35	18.2
Ammonia Oxidation	Joliet AAP	1.41	--	-	(2,750 ppm)	-
Ammonia Oxidation	Volunteer AAP	1.96	Mg of 60% HNO_3	-	8.15	92.7

(Continued)

Table 11. *(Continued)* GASEOUS EMISSIONS FROM AMMONIA OXIDATION PLANT PROCESSES

Source	Source Location	Exit Gas Flow Rate m^3/s	Emission Unit	kg/unit HNO_3	kg/unit NO_x	Annual Prod. Gg
Ammonia Oxidation	Volunteer AAP	1.96	Mg of 60% HNO_3	-	4.9	72.8
Ammonia Oxidation	Radford AAP	1.89	Mg of 100% HNO_3	-	3.2	81.8
Ammonia Oxidation	Radford AAP	-	--	(1,240 ppm)		
Ammonia Oxidation	Holston AAP	2.12 @ 55°C	Mg of 61% HNO_3		39.0	30.6
During Startup	Holston AAP	0.500 @ 55°C	--	-(19,300 ppm)		
Common Header	Holston AAP	0.001 @ 38°C	--	-(3,100 ppm)		

[a]Not operating at the present time.
[b]Equipped with a catalytic afterburner.
[c]Equipped with a tray-type gas absorption tower.
[d]Maximum design value.
[e]No_x controlled with an extended absorption tower.
[f]Equipped with a molecular sieve control system.

Source: Nelson, T. P. and R. E. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319, Task 50, July 1976.

Table 12. WASTE-WATER VOLUMES FROM AOP (HOLSTON AAP)

Source	Volume, m^3/day	Comments
1. Ammonia Purge Pot Blowdown	174	Approximately 40 kg/day NH_3.
2. Ammonia Vaporizer Blowdown	not measured	Approximately 190 kg/day NH_3.
3. Absorption Column Blowdown	not measured	Approximately 50.8 kg/day HNO_3.
4. Absorption Column Demister Blowdown	0.02	pH 0.1, TOC 28 mg/l, COD 95 mg/l, NH_3-N 37.2 mg/l, NO_3 + NO_2-N 100,000 mg/l.
5. Floor Washdown	5.5	
6. Steam Condensate	28.4	
7. Cooling Water	5450	
Total	5640	
Cooling Water, %	<96.3	
Process Waste, %	> 3.7	

Note: Production rate of 0.181 Gg/day equivalent 100% nitric acid.

Source: American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D. C., Oct. 1975.

ph, AOP process effluent will contain appreciable quantities of nitrate and ammonia nitrogen. Current treatment of waste-waters, where performed, consists solely of pH adjustment.

6. EPA Source Classification Code -

Ammonia Oxidation Process (old method): 3-01-013-01
Ammonia Oxidation Process (new method): 3-01-013-02

7. References -

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Expolsives and Propellants Production Industry. 3 Vols. Washington, D. C., Oct. 1975.

2) Environmental Protection Agency, Mid-Atlantic Region, Report on Waste Disposal Practices, Radford Army Ammunition Plant, Radford, Virginia, Philadelphia, Pa., May 1973.

Nitric Acid Concentration (NAC)

1. Function - The standard nitric acid concentration (NAC) process is a continuous operation in which weak nitric acid is distilled in the presence of sulfuric acid. Weak (60-65%) HNO_3 and concentrated H_2SO_4 are fed to the distillation tower along with steam. The sulfuric acid combines with free water while HNO_3 vapors (98-99%) form an overhead stream. The nitric acid vapors, contaminated with small amounts of NO_x and O_2 from HNO_3 dissociation, pass to a bleacher and condenser. The HNO_3 vapors condense as 95-99% HNO_3, while NO_x and oxygen pass to an absorber column for conversion to and recovery of additional weak nitric acid. This weak acid is recycled to the dehydrating unit. The still bottoms, consisting of approximately 68% H_2SO_4, are recovered and sent to a concentration unit for reprocessing. In an alternate method, used in one military production plant, weak HNO_3 from the AOP is mixed with hot concentrated aqueous magnesium nitrate. The hot mixture is passed through a stripping column; 99% HNO_3 is distilled off; and spent magnesium nitrate is drained off, reconcentrated and recycled.

2. Input Materials - Dilute nitric acid from the AOP (Process No. 1) or SAR (Process No. 3) constitutes the primary feed stream to this process. Concentrated sulfuric acid or magnesium nitrate solution may be used as dehydrating agents.

3. Operating Parameters - Specific data relating to flow rates, temperatures, pressures and equipment were not found in sources consulted for this study.

4. Utilities - Data were not available in sources consulted for this study.

5. Waste Streams - Absorber tail gas is the principal source of NO_x emissions from the nitric acid concentration process. In the National Emission Data System listing, emission factors range from 0.1 to 2.5 g NO_x/kg HNO_3 produced. The NO_x content of tail gas is affected by several variables. Elevated NO_x emissions may be caused by insufficient air supply or high temperatures in the absorber tower, exceeding design capacities for the system and internal leaks which permit gases from AOP to enter the tail gas system. A summary of gaseous emissions data from NAC at three commercial facilities and seven Army ammunition plants is presented in Table 13. Only three of the AAPs are currently in operation.

Because of a general lack of data on liquid process effluent from either AOP or NAC operations, definition of pollutant levels is difficult. Data on combined flows from several AOP and NAC facilities are available, however, and are presented in Table 14. The table presents data from commercial as well as military production plants. The data presented show considerable variability, due primarily to the extent of dilution of process effluents with non-contact waters. Nevertheless, it is readily apparent that low pH, high ammonia and nitrate nitrogen, and high sulfate levels are characteristic of effluents from NAC facilities. Where employed, treatment consists of acid neutralization and calcium sulfate sludge removal.

Table 13. GASEOUS EMISSIONS FROM NITRIC ACID CONCENTRATION PROCESSES

Source	Source Location	Exit Gas Flow Rate m^3/s	Emission Unit	kg/unit HNO_3	kg/unit NO_x	Annual Prod. Gg
HNO_3 Concentrators	Holston AAP	-	--	-	-	0^a
HNO_3 Concentrators	Holston AAP	0.0014	Mg Conc. HNO_3	-	4.55	28.8
HNO_3 Concentrators	Holston AAP	-	--	-	-	0^a
HNO_3 Concentrators	Holston AAP	-	--	-	-	0^a
HNO_3 Concentrators	Sunflower AAP	N/A	Mg Conc. HNO_3	-	0.5	0
HNO_3 Concentrators	Joliet AAP	-	Mg of TNT	-	2.0	80.1 (TNT)
HNO_3 Concentrators	Newport AAP	-	Mg of TNT	-	0.63	4.35 (TNT)
HNO_3 Concentrators	E. I. Dupont	-	--	-	497 Mg/yr	
HNO_3 Concentrators	Badger AAP	0.15	Mg Conc. HNO_3	-	3.9	49.7^b
HNO_3 Concentrators	Radford AAP	0.094	Mg Conc. HNO_3 (100%)	0.025	3.9	41.4
HNO_3 Concentrators	Holston AAP	0.083 @ 76°C	Mg Conc. HNO_3 (99.5%)	-	6.2	19.4
HNO_3 Concentrators	Holston AAP	-	--	-	(32,800 ppm)	-
HNO_3 Concentrators	Atlas Ch. Co. Allentown, PA.	0.00073	Mg-Explosives Produced	-	1.8	46.1 (Explosives)
HNO_3 Concentrators	Volunteer AAP	-	Mg of TNT	-	2.0	66.2
HNO_3 Concentrators	Holston AAP	0.11	Mg-Explosives	0.22	5.9	16.3

(Continued)

Table 13. (Continued) GASEOUS EMISSIONS FROM NITRIC ACID CONCENTRATION PROCESSES

Source	Source Location	Exit Gas Flow Rate m^3/s	Emission Unit	kg/unit HNO_3	kg/unit NO_x	Annual Prod. Gg
HNO_3 Concentrators	Holston AAP	0.11	Mg-Explosives	0.22	5.9	16.3
HNO_3 Concentrators	Holston AAP	0.11	Mg-Explosives	0.22	5.9	16.3
HNO_3 Concentrators	Holston AAP	0.11	Mg-Explosives	0.22	5.9	16.3
HNO_3 Concentrators	Radford AAP	26.5 @ 157°C	Mg-Conc. HNO_3	-	16.7	97.9
HNO_3 Concentrators	E. I. DuPont	-	--	-	57 Mg/yr	-
HNO_3 Concentrators	Radford AAP	10.8	Mg-Conc. HNO_3	0.5	-	49.9 (HNO_3) 22.7 (H_2SO_4)
HNO_3 Concentration	Radford AAP	0.11	--	-	(7,700 ppm)	-
HNO_3 Concentration	Radford AAP	0.12	--	(445 ppm)	(20,100 ppm)	
Conc. HNO_3 Holding Tank	Radford AAP	0.012	Mg-Conc. HNO_3	-	(30,800 ppm)	-
Weak HNO_3 Storage	Holston AAP	Nil	--	-	(32,500 ppm)	-

[a]Not operating at the present time.
[b]Maximum design value.

Source: Nelson, T. P. and R. E. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319, Task 50, July 1976.

Table 14. COMPARISON OF CHARACTERISTICS OF COMBINED WASTEWATERS FROM AOP PLUS NAC FACILITIES

Parameter	Joliet AAP Areas 1 & 2	Joliet AAP Area 3	Radford AAP	Holston AAP	Commercial Explosive Plants
Flow, m^3/day	80,240	42,392	NA	14,761	1,854
pH	7.2	2.7	NA	NA	2.3-3.1
BOD, mg/ℓ	NA	10	13	7.2	13.5
COD, mg/ℓ	NA	40	46	19.4	208
NH_3-N, mg/ℓ	NA	NA	1.2	0	191
NO_3 + NO_2-N, mg/ℓ	26	6.8	163	94	206
Sulfate, mg/ℓ	373	320	NA	NA	312

NA = Data not available

Source: American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

6. EPA Source Classification Code - HNO_3 Concentrators (TNT process): 3-01-010-02
HNO_3 Concentration (old method): 3-01-013-03
HNO_3 Concentration (new method): 3-01-013-04

7. References -

American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

Spent Acid Recovery (SAR)

1. Function - Spent acid from various nitration processes flows into the top of a denitrating tower. Steam, fed in at the bottom, rises through the tower stripping HNO_3 and NO_x from the spent acid. During recovery of spent, mixed acid, the still bottoms which contain diluted sulfuric acid are sent to the H_2SO_4 concentrator. Sulfuric acid (93%) from the concentrator is a by-product of most nitration processes. In some cases it can be recycled to oleum production or sold; depending on the source of the spent acid (nitration process), contamination with nitrobodies may limit its marketability.

In the bleacher the nitrogen compounds are further oxidized and/or condensed as nitric acid. Reflux of the condensate absorbs more NO_x, increasing the yield of acid which is then withdrawn, concentrated, and recycled to the nitration process. Uncondensed gaseous materials from the reflux column are routed through an absorption column where they are scrubbed with dilute HNO_3. Further oxidation of NO occurs, generating additional HNO_3 which is recycled to the denitrator tower.

2. Input Materials - The main feed stream to the acid recovery process consists of spent acid from various nitration processes. This spent acid is usually a mixture of dilute HNO_3 and H_2SO_4 and may also contain nitrosylsulfuric acid and nitrobodies. Steam and air in quantities not specified comprise the other feed streams to this process.

3. Operating Parameters - Specific data on operational temperatures or pressures have not been found in sources consulted for this study. One source indicates a total process capacity for a typical recovery unit of 0.018 Gg/hour with a feed input of 0.018 Gg/hour of spent acid.

4. Utilities - No specific data for water or energy consumption were found in the sources consulted during the study of this process.

5. Waste Streams - Waste waters from SAR units processing spent acid from TNT production may be considered typical of SAR waste waters in general. They are characterized by high dissolved solids content, on the order of 11 kg/Mg of TNT production, sulfates (4 kg/Mg TNT) and small quantities of nitrogen salts. One source indicates that limited observation of one spent acid recovery unit showed no apparent problems with atmospheric emissions from the denitrating tower even though the unit has no emission control equipment. However, the same source states that a dark orange plume is continually emitted from the stack of nitric acid concentrators indicating a high concentration of NO_x, estimated to be on the order of 9.8×10^5 kg/year. The National Emission Data System emission factor for HNO_3 concentrators indicates a level of 2.0 mg NO_x/kg TNT produced. Factors for H_2SO_4 regeneration indicate 7.5 mg SO_x and 1.0 mg NO_x/kg TNT. A summary of gaseous emission data from SAR including sulfuric acid regeneration and concentration operations is presented in Tables 15 and 16. The tables include data from one commercial facility and six Army ammunition plants, three of which are currently out of operation.

Table 15. GASEOUS EMISSIONS FROM SPENT ACID RECOVERY PROCESSES

Source	Source Location	Exit Gas Flow Rate m^3/s	kg/Mg spent acid HNO_x	kg/Mg spent acid NO_x	Annual Prod. Gg
Spent Acid Recovery	Radford AAP	0.377	0.006	0.8	5.80
Spent Acid Recovery	Sunflower AAP	0.644	NA	NA	88.74

[a]Equipped with a direct flame afterburner designed for 95% NO_x removal.

NA = Data not available.

Source: Nelson, T. P. and R. E. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319, Task 50, July 1976.

Table 16. GASEOUS EMISSIONS FROM SULFURIC ACID REGENERATION AND CONCENTRATION PROCESSES

Source	Source Location	Exit Gas Flow Rate m^3/s	Emission Unit	kg/unit SO_x	kg/unit H_2SO_4 Mist	kg/unit NO_x	Annual Prod. Gg
Regeneration							
Regeneration (40% Oleum)	Volunteer AAP	-	Mg of 40% Oleum	0.85	2.62	-	50.5
H_2SO_4 Regenerator	Joliet AAP	-	Mg of TNT	7.5	0.012	-	80.1
H_2SO_4 Regenerator	Newport AAP	-	Mg of TNT	2.08	-	0.42	4.35 (TNT)
H_2SO_4 Regenerator[a]	Austin Powder McArthur, Ohio	-	--	-	-	151 Mg/yr	-
H_2SO_4 Regenerator	Volunteer AAP	16.5 @ 29°C	--	215 Mg/day	662 Mg/day	-	-
H_2SO_4 Regenerator	Volunteer AAP	16.5 @ 29°C	--	215 Mg/day	662 Mg/day	-	-
H_2SO_4 Regenerator	Volunteer AAP	16.5 @ 29°C	--	215 Mg/day	662 Mg/day	-	-
H_2SO_4 Regenerator	Radford AAP	0.511 @ 28°C	Mg of Oleum	28.6	neg.	-	34.3
H_2SO_4 Regenerator	Radford AAP	17.9	Mg of 40% Oleum	3.3	-	-	182
H_2SO_4 Regenerator[b]	Volunteer AAP	0.491	Mg of 100% H_2SO_4	2.6	0.75	2.0	137
H_2SO_4 Regenerator	Volunteer AAP	17.3	Mg of H_2SO_4	2.6	0.73	-	137
H_2SO_4 Regenerator	Volunteer AAP	15.8	Mg of H_2SO_4	35.8	0.62	-	165
H_2SO_4 Regenerator	Volunteer AAP	-	--	278 ppm	-	-	162
H_2SO_4 Regenerator	Volunteer AAP	-	--	240 ppm	-	-	177
Concentration							
H_2SO_4 Concentrator[c]	Sunflower AAP	-	Mg of 93% H_2SO_4	0.64	2.06	1.14	82.8
H_2SO_4 Concentrator	Volunteer AAP	7.55	Mg of 93% H_2SO_4	0.32	0.04	0.08	49.7

(Continued)

Table 16. (Continued) GASEOUS EMISSIONS FROM SULFURIC ACID REGENERATION AND CONCENTRATION PROCESSES

Source	Source Location	Exit Gas Flow Rate m^3/s	Emission Unit	kg/unit SO_x	kg/unit H_2SO_4 Mist	kg/unit No_x	Annual Prod. Gg
Concentration (Continued)							
H_2SO_4 Concentrator[d]	Sunflower AAP	8.40	Mg of 100% H_2SO_4	2.6	9.4	-	76.2
H_2SO_4 Concentrator[d]	Joliet AAP	5.28	--	65 ppm	1.7 ppm	-	-
Oleum Production							
Oleum Plant	Sunflower AAP	5.14	Mg of 100% H_2SO_4	6.3	0.48	-	82.8
Oleum Plant	Joliet AAP	-	--	2,920 ppm	36 ppm	-	-
Oleum Plant	Joliet AAP	3.59	--	2,510 ppm	5 ppm	-	-
Oleum Plant	Radford AAP	1.94	Mg of 40% Oleum	27.6	0.6	-	34.7
Oleum Plant	Radford AAP	1.83	--	2,080 ppm	390 mg/m^3	-	-
Oleum Plant	Badger AAP	6.13	Mg of 40% Oleum	17.9	-	-	82.8

[a]A No_x condenser is located upstream.
[b]After a Na_2CO_3 scrubber.
[c]Currently inoperative.
[d]Before an electrostatic precipitator.

Source: Nelson, T. P. and R. E. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319, Task 50, July 1976.

6. EPA Source Classification Code - Source Classification Codes for spent acid recovery processes have been established only for those considered part of TNT production processes. These are: HNO_3 Concentrator: 3-01-010-02
H_2SO_4 Regeneration: 3-01-010-03

7. References -

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

2) Environmental Protection Agency, Mid-Atlantic Region. Report on Waste Disposal Practices, Radford Army Ammunition Plant, Radford, Virginia. Philadelphia, Pa., May 1973.

TNT Production Processes

The production of TNT follows the same chemical process, regardless of variations in physical facilities or manufacturing methods. Liquid toluene is nitrated by treatment with mixed nitric and sulfuric acids. Following the nitration reaction, undesirable isomers as well as residual dinitrotoluene (DNT) are removed by conversion to soluble salts and extraction.

Figure 5 is a flow chart for TNT production. Three processes are described: Nitration (Process No. 4), Purification (Process No. 5), and Finishing (Process No. 6).

The nitration process is descriptive of both batch and continuous production methods. The continuous production process is merely a modernized version of batch production. As developed by Canadian Industries, Limited (CIL), nitration is carried out in six nitrator-separator stages with the organic phase flowing countercurrent to the acid phase. The CIL process, like all continuous processes, features smaller inventories of explosive material at any stage in the production line. It also features more efficient control of process conditions and better utilization of recycle streams, resulting in some reduction in waste stream generation.

Purification (Process No. 5) is likewise descriptive of both batch and continuous processes. As in nitration, the CIL purification operation is an improvement over batch operation but the principle and chemistry remains the same. In the CIL process countercurrent washing and sellite treatment in multiple stages provides a more efficient utilization of the reagents used for purification. The CIL process differs from batch purification mainly in that 1) water is used in place of sodium carbonate solution for initial removal of free acid and 2) sellite is prepared directly from dry sodium sulfite rather than through the SO^2-carbonate reaction. Finishing operations are identical for both batch and continuous processes.

Dinitrotoluene (DNT) may be prepared in a TNT plant, but at present all DNT used in military propellant formulations is purchased from commercial sources. When toluene is subjected to dinitration (see Process No. 4) the "bi-oil" produced contains approximately 75 percent of the 2, 4-isomer. Dinitrotolune produced commercially is removed from the reaction at this point, washed free of acid and sold. A complete description of DNT production processes appears in Chapter 6, Industrial Organic Chemicals, Part 2.

When used in propellant manufacture, DNT is purified by fractional freezing or "sweating." Purification of DNT is essentially a pollution-free operation because the separated impurities are all fed to the TNT manufacturing operation for conversion to TNT. Aqueous effluents are limited to uncontaminated cooling water. For these reasons, and because DNT is an interim product in TNT manufacture, process descriptions for DNT manufacture are not included in this study.

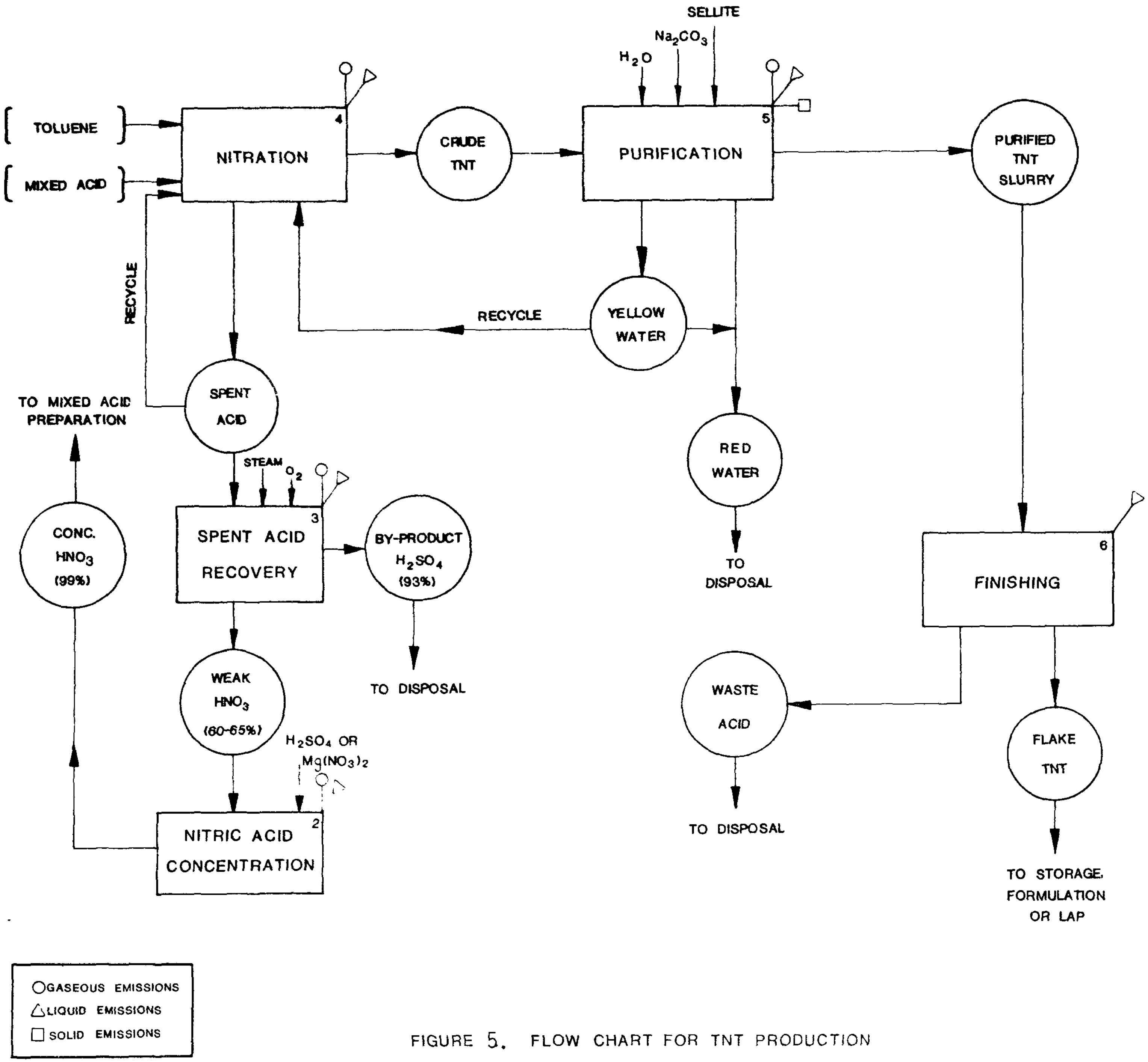
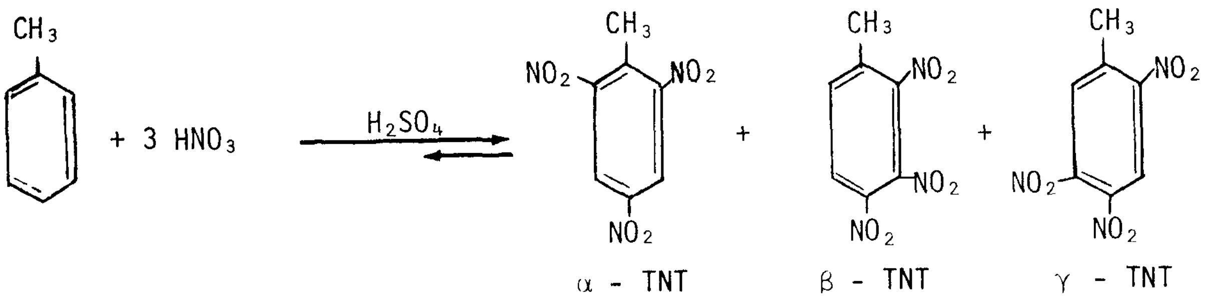


FIGURE 5. FLOW CHART FOR TNT PRODUCTION

Nitration

1. Function - The production of TNT by nitration of toluene is a three-step process, performed in a series of reactors. The mixed acid stream flows countercurrent to the flow of the organic stream during the process, as illustrated in Figure 6. It can be seen that the mixed acid stream in its most concentrated state is fed to the last reactor and emerges as spent acid from the first reactor.

The overall chemical reaction may be illustrated by the following schematic equation.



(4-1)

Feed chemicals to the first reaction step consist of toluene and spent acid from dinitrotoluene production, fortified with a 60% HNO_3 solution. Heat exchange coils in the reaction vessel control the temperature of the exothermic mononitration. The predominant product is ortho-nitrotoluene but the meta-and para-isomers are also formed.

The organic layer, often called "mono-oil," is decanted and pumped to the second reactor.

The "mono-oil" is subjected to further nitration with acid from the third reactor fortified with additional HNO_3. During the continuous flow (CIL) production process, a recycle stream known as "yellow water" joins the process stream in the second reactor.

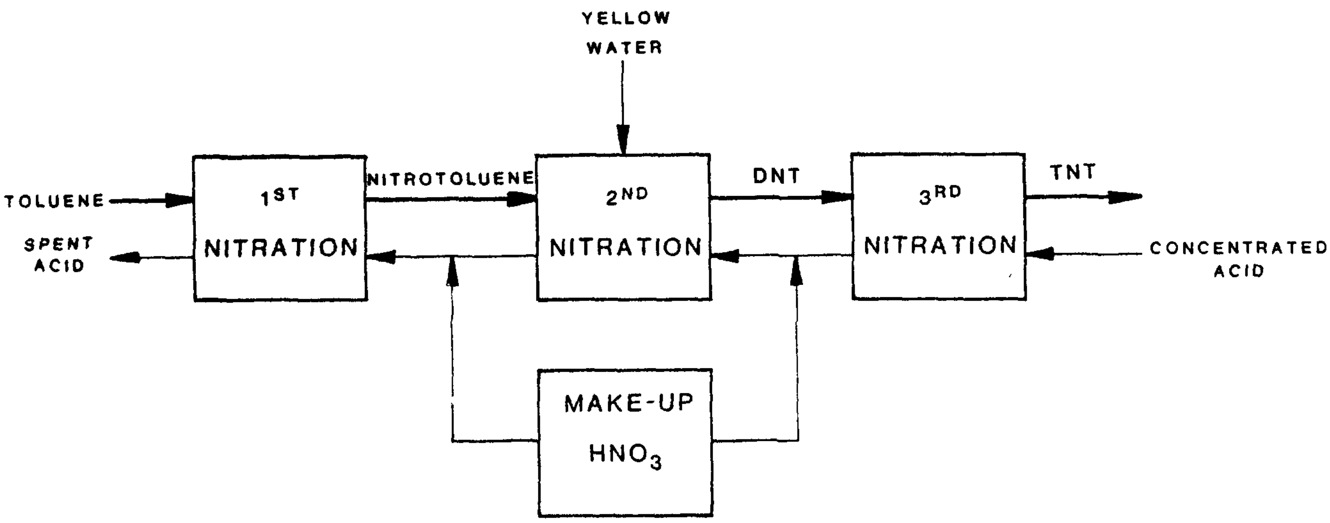


FIGURE 6. NITRATION OF TOLUENE TO FORM TRINITROTOLUENE

The organic product from the second nitration step, known as "bi-oil," consists of a mixture of all possible isomers of dinitrotoluene (DNT). The "bi-oil" is pumped to the third reactor.

The final nitration is accomplished by treatment of the "bi-oil" with a fresh feed acid mixture of nitric acid and oleum. The crude TNT from this third nitration consists primarily of 2,4,6-trinitrotoluene (α-TNT) contaminated with small quantities (approximately 5%) of the β or 2,3,4- and γ- or 3,4,6-isomers.

The crude mixture is purified in Process No. 5.

2. <u>Input Materials</u> - Basis - 1.0 kg crude TNT

Toluene - 0.458 kg

Nitric Acid - 0.57 kg. This figure is not corrected for HNO_3 replenishment or "butting up" in the first and second nitrators. Concentrated (98%) HNO_3 is used in the preparation of the mixed-acid feed stream which enters the reaction in the third nitration step. Spent acid from this step is fortified with 60% HNO_3 and used as feed acid for the second nitrator. Spent acid from the second step is again fortified with 60% HNO_3 and feeds the first nitrator.

Sulfuric Acid - 1.858 kg - oleum (109% sulfuric acid) is used as the second component to the binary mixed acid which is fed to the reaction in the third nitration step. As one of the constituents of the spent acid from trinitration, the diluted H_2SO_4 feeds the second nitration step and subsequently, the first nitration.

The composition of the mixed acid as it moves through the process is shown in Table 17.

Table 17. ACID COMPOSITION IN THE THREE NITRATION REACTORS

Reactor	HNO_3	H_2SO_4	$ONOSO_3H$	Nitrobodies	Water
1	14%	48%	17%	2%	19%
2	13%	54%	18%	8%	8%
3[a]	23%	83%	-	-	-

[a]The total is greater than 100% because the oleum is 109% based on SO_3 analysis.

Yellow Water - quantities unknown - A dilute solution composed of crude TNT in water and acids from the first crystallization and water wash in the CIL purification process is recycled to the reaction in the second nitration step of the CIL continuous flow process.

3. Operating Parameters - Temperature Control: Temperature control data for continuous flow (CIL) production of TNT were not found in the sources consulted for this study. In the batch production process the mono-mix acid is cooled to 36 to 38°C. Toluene is added under the surface of the acids and the exothermic reaction mixture is cooled sufficiently to hold the temperature at about 40°C during addition. The temperature of the reaction mixture is then allowed to increase to 57 to 60°, where it is held for one hour. The mixture is then cooled to 38°C and the mono-oil is separated from the spent acid. In the second nitration the mono-oil is added to bi-mix acid which has been cooled to 77°C. Upon addition of mono-oil the reaction mixture warms to 82 to 85°C, where it is "cooked" for 8 minutes and then is cooled to 77°C. The tri-mix acid is cooled to 80°C. Bi-oil is added at a rate sufficient to cause a temperature increase of 0.5°C/min, to a maximum of 90°C. After being held at that temperature for several minutes, the mixture is allowed to warm at the rate of 1°C/min to 110°C. Temperature is maintained at that level for 20 minutes, then cooled with continuous stirring to 107°C. Stirring is discontinued, and the temperature is reduced to approximately 93°C as the tri-oil or crude TNT is allowed to separate from the tri-spent acid.

Pressure: The reaction occurs at atmospheric pressure.

Flow Rate: A typical line for continuous flow production of TNT yields approximately 44,000 kg/day purified explosive with an input of 20,150 kg toluene, 25,430 kg nitric acid and 82,850 kg sulfuric acid. A typical batch production line at full operation can produce 45,830 kg/day purified explosive. Data specifying batch size were not found in sources consulted for this study.

Miscellaneous: Sulfuric acid acts to catalyze the nitration of toluene by forming a hydrated molecule with the water of reaction, thus shifting the reaction equilibrium to the right.

4. Utilities - Water: Based on reported total water usage for a typical continuous-flow TNT production facility of 19,492 m^3/day at 131.5 Mg/day production (18,925 m^3 cooling + 567 m^3 process) total water usage corresponds to 0.148 m^3/kg of refined product. Details of water usage for individual processes have not been found in sources consulted for this study.

Electricity: No data available.

Fuels: No data available.

5. Waste Streams - Gaseous emissions from the nitrators and separators, containing CO, CO_2, NO, NO_2, N_2O and trinitromethane (TNM), are passed through a fume recovery system for recovery of NO_x as nitric acid, then vented through scrubbers to the atmosphere. Final emissions contain quantities of unabsorbed NO_x as well as TNM. One reference source indicates rated capacity for a typical fume recovery system operation as part of a continuous flow production line as 272 kg HNO_3 per hour. The same source, however, indicates that a visible orange plume is emitted from the vent stack during operation and that an estimated 245 Mg/year of NO_x are discharged to the atmosphere. Table 18 presents summary emission data for acid fume recovery (AFR) systems at three Army ammunition plants. Only two of the plants listed are currently in operation (Radford and Volunteer) and only Volunteer is currently engaged in TNT production.

Table 18. GASEOUS EMISSIONS FROM TNT MANUFACTURING PROCESSES

Source	Source Location	Exit Gas Flow Rate (m^3/s)	kg/Mg TNT HNO_3	kg/Mg TNT NO_x	Annual Prod. (Gg)
TNT Nitrators[a]	Volunteer AAP	Unk	-	11.3	24.7
TNT Nitrators	Joliet AAP	-	-	80	80.1
TNT Nitrators (out of the AFR)	Volunteer AAP	3.86	-	27.5	20.2
TNT AFR Outlet	Joliet AAP	0.347	(11,400 ppm)		-
TNT AFR Outlet	Volunteer AAP	0.326	(64,600 ppm)		-
TNT AFR Outlet	Radford AAP	0.335	(210 mg/m^3)	(4,150 ppm)	-
TNT AFR Outlet					
W/O Combustor	Volunteer AAP	3.86	-	27.5	21.8
W/Combustor	Volunteer AAP	-	-	(235 ppm)	21.8
TNT AFR[a]	Volunteer AAP	2.36	-	9.6[b]	0.304
TNT AFR Inlet	Joliet AAP	0.359	-	(19,700 ppm)	-

[a]Equipped with a tray-type gas absorption column (90-99% removal of NO_x).

[b]Maximum expected value will be near 13.9 (8 per Mg of TNT produced).

Sources: Nelson, T.P. and R. E. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Industry Radian Corp. EPA Contract 68-02-1319, Task 50, July 1976.

Waste-water generated during the nitration-separation process consists primarily of cooling water from the reactor vessels. Process water, for the most part, is carried through acid recovery and discharged following that process. No data on waste-water from fume recovery systems have been found in sources consulted for the study.

6. EPA Source Classification Code - Nitration Process: 3-01-010-01

7. References -

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

2) Davis, Tenney L. The Chemistry of Powder and Explosives. N.Y., Wiley, 1941, 1943.

3) Environmental Protection Agency. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Explosives Manufacturing Point Source Category. EPA 440/1-76/060-j, Group II. Washington, D.C., March 1976.

4) Environmental Protection Agency, Mid-Atlantic Region, Report on Waste Disposal Practices, Radford Army Ammunition Plant, Radford, Virginia. Philadelphia, Pa., May 1973.

5) Explosives. In: Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 8. H. F. Mark, ed. N.Y., Wiley, 1966, pp. 581-718.

6) Processes Research, Inc. Air Pollution from Nitration Processes. Contract No. CPA 70-1, Task 22. Cincinnati, Ohio, March 1972.

Purification

1. Function - Following nitration, crude TNT is washed with water to remove free acid. In the batch process neutralization with soda ash (Na_2CO_3) is the first step, followed by water washes. In the continuous process the crude TNT is subjected to a series of water washes, the water flowing countercurrently to process flow. The TNT is then neutralized with soda ash and treated with a 16% aqueous sodium sulfite (sellite) solution to remove contaminating isomers. A single sellite treatment is used for batch production while a double, countercurrent treatment with the sellite solution occurs during continuous production. Sellite (Na_2SO_3) purification is accomplished by the replacement of the nitro group in the meta-position in β- and γ-TNT by a sodium sulfonate group, forming highly soluble sodium salts of the corresponding dinitrotoluenesulfonic acids. The sellite also reacts with a small quantity of γ-TNT forming hexanitrobibenzyl, giving the red color. The sellite-treated TNT receives a final series of countercurrent extractions with water and is transferred to the finishing process as a slurry. Water from these extractions, combined with the sellite solution, constitutes the "red water" which is concentrated and either sold to the paper industry or evaporated to dryness and incinerated.

2. Input Materials - Basis - 1.0 kg purified TNT.

Crude TNT - 1.1 kg - product of the nitration process, contaminated with 3 to 5% β- and γ-TNT isomers and residual nitration acids.

Soda Ash - 0.06 kg - 3% solution in water.

Na_2SO_3 - 0.06 kg - as sellite (16% Na_2SO_3 in water). This is usually prepared by burning sulfur to produce SO_2 and countercurrent scrubbing to remove the trioxide and other impurities. This is followed by reaction with 22% Na_2CO_3 in a countercurrent packed tower with recirculation to achieve process strength. (In CIL continuous nitraton process, sellite is prepared directly from dry Na_2SO_3.)

Process Water - 0.89 ℓ.

3. Operating Parameters - Sources consulted for this study were devoid of information relating to process temperatures, flow rates, or operating pressures.

4. Utilities - Fuel: Red water incineration at one production facility, processing over 10.4 Gg/yr of red water, uses natural gas as a primary fuel at a rate of 19,600 m^3/month.

Water: Data from one facility producing TNT by the continuous flow method indicates, for TNT purification, total process water use is 0.89 ℓ/kg TNT. Of this, approximately 0.09 ℓ/kg becomes yellow water which is returned to the continuous nitration line and 0.44 ℓ/kg occurs as red water from the sellite wash. The balance is scrubber water.

Data relating to the consumption of other utilities in the purification of TNT have not been found in the sources consulted for this study.

5. Waste Streams - Waste water is generated from three sources described below.

Yellow water: The acidic effluent from the first water washing of crude TNT during continuous flow production is returned to the nitration process at the dinitration step. Excess yellow water, above the volume returned to nitration, is combined with other waste process water for treatment.

Red Water: The effluent from sellite treatment and subsequent washing of crude TNT has a typical composition of 77.6% water, 17.3% organics, 5.2% $NaNO_x$, and 2.9% Na_2SO_x. (Due to conflicting analytical methods, the total exceeds 100%.) The production of red water amounts to 0.34 kg/kg TNT produced, consisting of 0.26 kg process water, 0.06 kg organics (nitrotoluenes and nitrotoluenesulfonic acid salts), and 0.02 kg dissolved inorganics ($NaNO_x$ and Na_2SO_x).

Red water is concentrated to 35 to 40% solids and either sold to the paper industry as a source of sulfite liquor or incinerated. Incineration results in atmospheric emissions of NO_x and SO_2 as well as solid waste (ash). It is reported that, at one facility producing TNT by batch nitration, 0.179 kg ash is produced/kg TNT manufactured. The ash, consisting primarily of Na_2SO_4 is disposed of in sanitary landfills or by stockpiling on open land. The ash, reported to be 90% soluble, is susceptible to leaching by rain water, creating a potential source of contamination to surface as well as ground water.

Pink Water: This waste stream is generated by the TNT manufacturing process as well as by LAP operations. Pink water from manufacturing plants arises from nitration fume scrubber discharge, red water concentration distillates, finishing operation hood scrubber and washdown effluents, and possibly spent acid recovery wastes. The first two sources of pink water may contain isomers of DNT as well as of TNT. One source indicates that nitrobody content in discharges from the TNT spent acid recovery plant at Radford AAP ranged from 15 to 168 kg/day. Laundry waste waters have also been reported to contain TNT. Table 20 summarizes available data on nitrobody content of pink waters from various sources. Pink waters currently are discharged to sumps to remove settleable solids. Effluent from the sumps may be treated by carbon adsorption or by evaporation/leaching. Sludge from the sumps is removed at regular intervals and disposed of by open burning.

The National Emission Data System emission factor listing indicated 16 g particulates, 1 g SO_x and 19 g NO_x emissions/kg TNT produced as a result of red water incineration. Exhaust emissions from sellite manufacture are factored at 0.35 g/kg TNT produced. Table 19 presents available emission data from miscellaneous sources at the only Army ammunition plant currently engaged in TNT production.

6. EPA Source Classification Code - Sellite exhaust: 3-01-010-06
Red water incineration: 3-01-010-04

Table 19. MISCELLANEOUS GASEOUS EMISSION SOURCES FROM TNT MANUFACTURING PROCESSES

Source	Source Location	Exit Gas Flow Rate (m^3/d)	kg/Mg TNT SO_x	kg/Mg TNT Acid Mist	kg/Mg TNT NO_x	Annual Emissions (Gg)
TNT Manufacturing						
Acid Wash[a]	Volunteer AAP	1.93	-	-	neg.	0.303
Wash	Volunteer AAP	-	-	-	80	82.7
Sellite Wash[a]	Volunteer AAP	Unk	neg.	-	-	0.303
Finishing Plant						
Air Collection System	Volunteer AAP	1.42	-	neg.	-	0.303

[a]Equipped with a gas scrubber (90 to 99% removal of particulates and SO_x).

Sources: Nelson, T. P. and R. E. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319, Task 50, July 1976.

Table 20. REPORTED TNT CONCENTRATIONS IN PINK WASTE WATERS

Plant	Evaporator Condensate mg/ℓ	LAP Cleanup mg/ℓ	Scrubber Water mg/ℓ	Laundry Wastewater mg/ℓ
Joliet AAP	1.4	178.3		
	3.7-6.1			
	4.4			
				2.9
	16			
NAD Crane				
Rockeye		40.1		
Plant A		5.8-11.2		
Plant B		20.2		
Holston AAP		3-9[a]	2-22	
Radford AAP	7.3			
		90-175		
		75		
NAD McAlester		30.6-38.4		
			30-80	
Iowa AAP		86.9		
				25.4
Milan AAP		<1		
Louisiana AAP		80		
Cornhusker AAP (inactive)		57		2.7

[a]From incorporation of TNT into Composition B.

Source: American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D. C., Oct. 1975.

7. References -

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D. C., Oct. 1975.

2) Booz-Allen Applied Research, Inc. A Study of Hazardous Waste Materials, Hazardous Effects and Disposal Methods. 3 Vols. Vol. II, PB 221-466, Bethesda, Md., 1973.

3) Environmental Protection Agency, Mid-Atlantic Region, Report on Waste Disposal Practices, Radford Army Ammunition Plant, Radford, Virginia. Philadelphia, Pa., May 1973.

Finishing

1. Function - TNT crystals from the purification process are slurried with water and pumped to a melt tank where the TNT is melted and most of the water is removed by evaporation. The molten TNT is then passed through hot air dryers for evaporation of residual water. The dehydrated product is then solidified on a water-cooled flaker drum or stainless steel belt. The solidified TNT is scraped from the belt or drum with a beryllium blade. The resultant flaked TNT is boxed and transferred to a storage or loading area.

2. Input Materials - Crystalline TNT from the final water wash in the Purification Process (No. 5) and process water are the input materials for finishing.

3. Operating Parameters - Hot air is supplied to dryers at 100°C or higher. Data on other operating parameters were not found in sources consulted for this study.

4. Utilities - Data were not found in sources consulted for this study.

5. Waste Streams - A waste-water stream results from this process. So-called "waste acid" from the finishing process results from spillage, floor drainage and washings from the finishing area. Effluent is treated with lime or soda ash to neutralize residual acids and discharged to the chemical sewer. A report of a study performed on waste acid treatment at one facility indicated overall performance of the treatment plant is inadequate.

Neutralization of acidic waste is adequate under normal conditions, but some waste parameters are not suited to treatment by such a neutralization facility. This is evidenced by an average effluent content of 13,254 kg/day dissolved solids, 245 kg/day NO_x, 1800 kg/day SO_x, 818 kg/day COD and 10.6 kg/day α-TNT.

Sources consulted for this study were not specific on dryer venting but it may be assumed that venting is to the atmosphere with water vapors the sole constituent of the waste stream.

6. EPA Source Classification Code - None exists for this process.

7. References -

(1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D. C., Oct. 1975.

(2) Environmental Protection Agency, Mid-Atlantic Region, Report on Waste Disposal Practices, Radford Army Ammunition Plant, Radford, Virginia. Philadelphia, Pa., May 1973.

3) Explosives. In: Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 8. H. F. Mark, ed. N. Y., Wiley, 1966, pp. 581-718.

Nitrocellulose (NC) Production Processes

Nitrocellulose (NC), or more properly cellulose nitrate, is a fibrous white solid resembling the cotton linters or wood pulp from which it is prepared. Nitrocellulose is generally graded or characterized according to the degree of nitration. Dry uncolloided cellulose nitrate is a violent and sensitive explosive. Treatment with selected plasticizers produces a colloidal dispersion of nitrocellulose molecules, rendering the material less sensitive and more prone to burning than to detonation.

The various grades of NC are used chiefly in manufacturing lacquers, plastic compositions and propellant powders, with only a small amount being used for the manufacture of gelatin-type dynamites. The inclusion of NC production in the explosives industry is predicated upon its suitability as a basic material for propellant formulation.

A flow chart for NC production is presented in Figure 7. Two processes are described: Nitration (Process No. 7) and Purification (Process No. 8).

Four different processes have been used historically for the nitration of cellulose. These are 1) the pot, 2) the Thompson displacement, 3) the centrifugal, and 4) the mechanical dipper processes. The mechanical dipper process, as described in Process No. 7, is the least hazardous, and is the only one now used in the United States. A newly developed continuous nitration processing line is currently being installed at one Army ammunition plant.

Gaseous emissions from NC production are generally associated with nitration of the cellulose molecule (Process No. 7) whereas liquid waste streams are generated mainly during purification.

Purification of NC, which is described in Process No. 8, is actually a chain of individual processes for treating and washing the fibrous product. Neutralization of reaction acids trapped within the cellular structure of NC is extremely difficult but is absolutely necessary to insure stability of the final product.

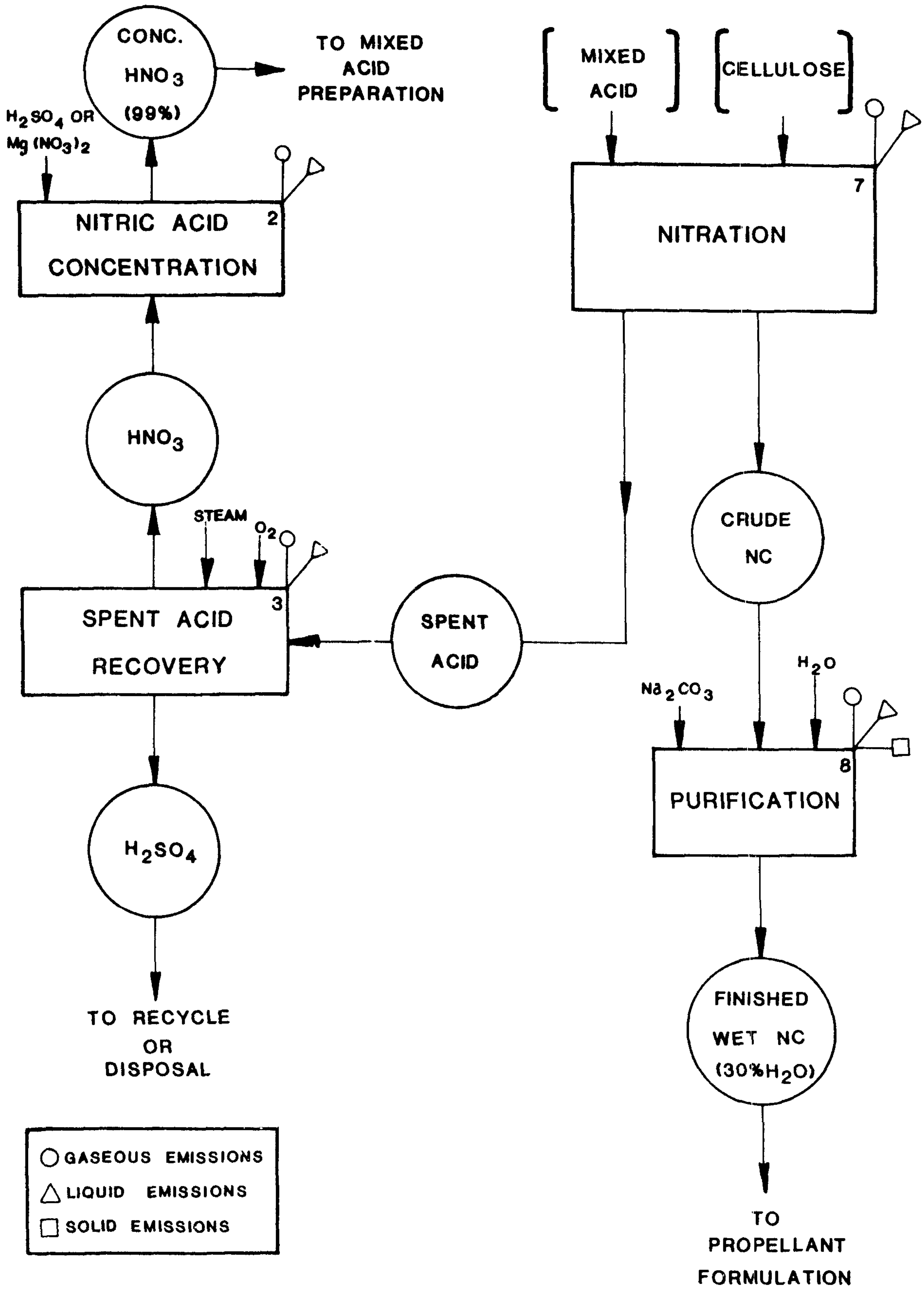
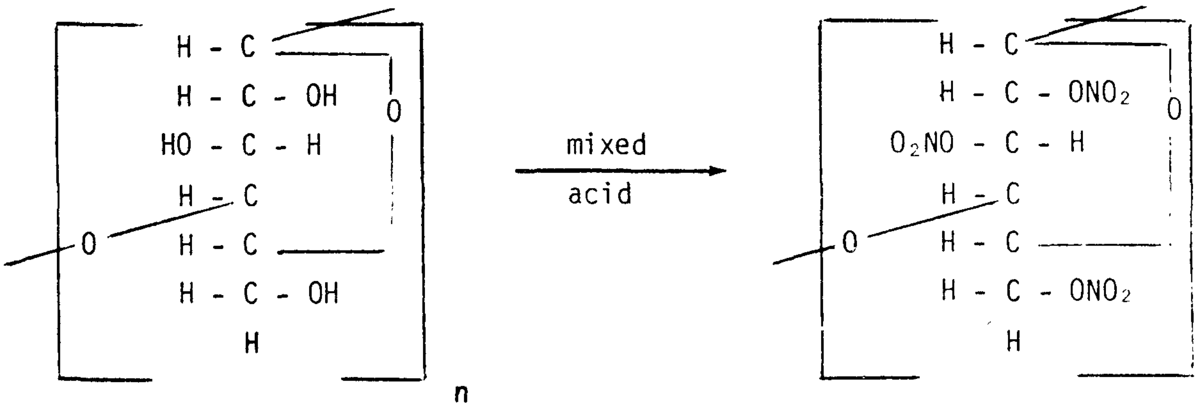


FIGURE 7. FLOW CHART FOR NITROCELLULOSE PRODUCTION

Nitration

1. Function - Raw cellulose (cotton linters or specially prepared wood pulp) must be purified for use. The raw material is first boiled with dilute caustic and then washed several times with water. This is followed by several bleachings with bleaching powder or sodium hypochlorite in water. After drying and shredding, the material is ready for the reactor.

In batch production pre-purified cotton linters or wood pulp (dry and shredded or fluffed) are added to mixed nitric and sulfuric acid in metallic reaction vessels known as "dipping pots" and the mixture is stirred with cooling to control temperatures of the exothermic reaction. The reaction is represented by the following idealized formula.



(7-1)

Theoretically, complete nitration of all hydroxyl groups would yield a final nitrogen content of 14.14%. In practice, nitrogen content is held to between 10.5% and 13.8%, representing a substitution of 1.8 to 2.9 hydroxyls per glucose anhydride unit in the chain. Substitution values are controlled by the proportions of the mixed acids used for nitration, the value varying directly with acid concentration.

Following nitration the crude NC is "wrung" in a centrifuge to remove most of the spent nitrating acids and then dumped into a "drowning tub" filled with water to stop the reaction. The crude NC/water slurry from the drowning tub is then transferred to the purification area.

2. Input Materials - Values for input quantities/unit of product are based on rated capacities for two production facilities of approximately 3818 kg NC/hr at 263 kg cellulose/hr feed input. Theoretical values may be calculated as 0.54 kg cellulose and 25.3 kg mixed acid/kg crude NC. Both rated and theoretical values are relative and will show some degree of variation, depending on acid ratios and level of nitration in the product.

Basis: 1.0 kg crude nitrocellulose as guncotton.

Pre-purified cellulose fibers (0.69 kg) and mixed acid (32.4 kg) constitute the feed stream to this process. The mixed acid is prepared from HNO_3 and H_2SO_4. The relative concentrations of acids control the extent of nitration and the nature of the resultant product, as illustrated in Table 21.

Table 21. REPRESENTATIVE MIXED ACIDS USED IN PREPARING VARIOUS GRADES OF NITROCELLULOSE

Product	Mixed Acid Sulfuric %	Nitric %	Nitrosylsulfuric %	Water %
Pyroxylin (8-12% N)	45	35	--	20
Pyrocellulose (12.6% N)	58	22.5	4	15.5
Guncotton (13.2-13.4% N)	60	26.5	4.5	10

3. Operating Parameters - Sources consulted indicated control of reaction temperature in the ranges of 30°C to 34°C as well as 37°C to 40°C. Reaction time for batch nitration in dipping pots is 25 minutes for the standard 15 kg batch. Continuous nitration lines produce crude NC at the rate of approximately 68 to 70 kg/min.

4. Utilities - No data for utilities consumption specific to the nitration process in NC production were found in the sources consulted for this study. See Figure 8 for a schematic of total daily water consumption for a typical NC batch facility at full production.

5. Waste Streams - The reactor and centrifuge (or wringer) are vented to an absorber where any NO_x is oxidized and absorbed in water. The weak HNO_3 solution thus produced is transferred to the acid concentration system. Concentrated acids from this system are recycled to the mixed acid system. Absorbers are vented to the atmosphere. Emissions consist of NO_x from the first absorber and NO_x + SO_x from the second. The National Emission Data System emission factor listing indicates 0.65 g SO_x and 1.05 g NO_x/kg NC emissions from the reactor pots with 32.5 g SO_x and 14.5 g NO_x from acid concentrators. Table 22 presents summary emission data from three army ammunition plants (GOCO), two of which are currently inactive. No quantitative data pertaining to solid or waterborne waste specific to the nitration process were found in the sources consulted for this study. Cleanup operations generate virtually all of the waste water from the nitration process. Thus, waste water may be expected to have a low pH and to contain relatively high levels of NO_3-N, and suspended solids.

6. EPA Source Classification Code - Reactor pots: 3-01-041-01
H_2SO_4 Concentrators: 3-01-041-02

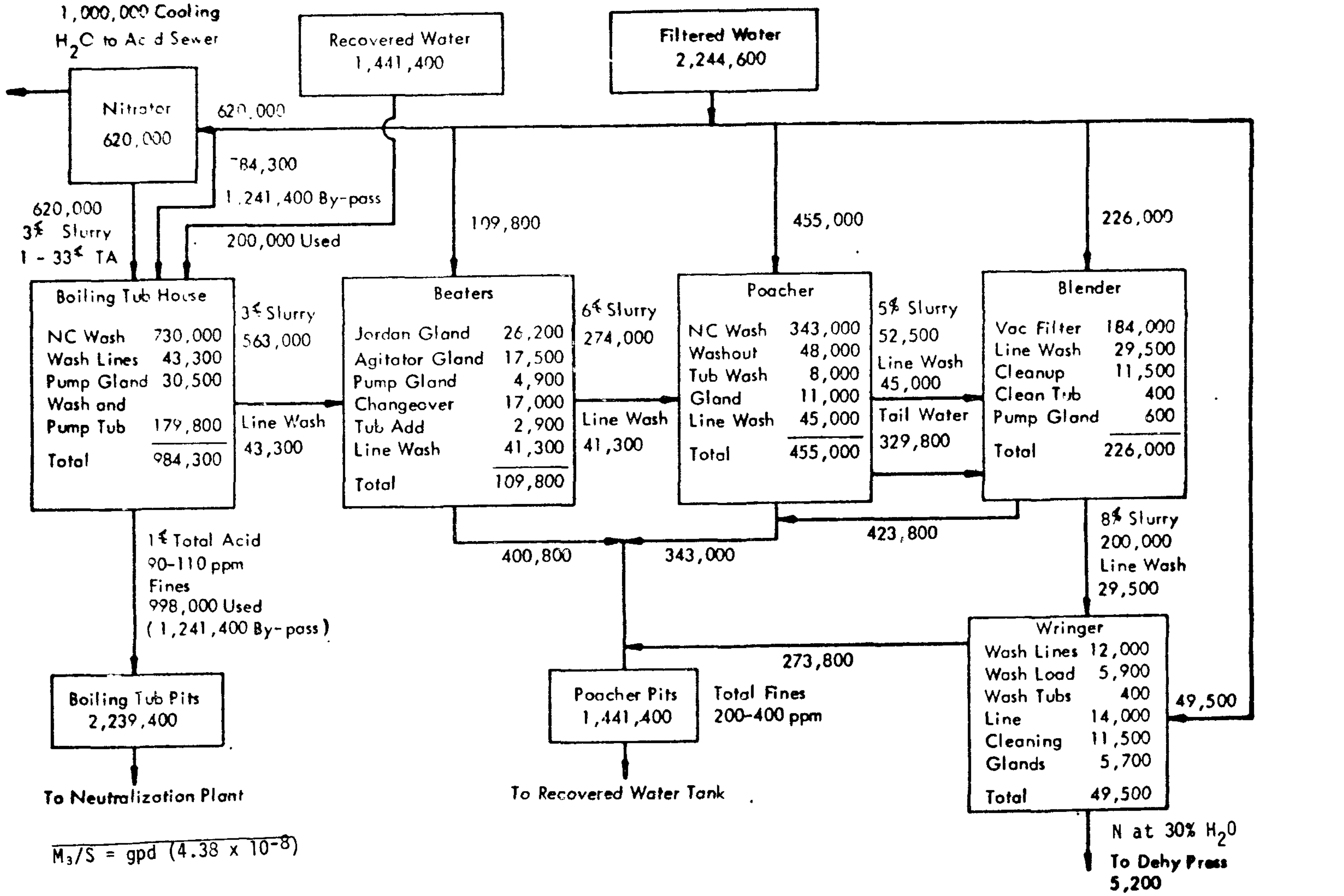


Figure 8. TYPICAL NC WATER USE (gpd) AT RADFORD AAP - ONE LINE NC CAPACITY; 144,000 LB (65.3 Mg)/DAY [PULP], OR 120,000 LB (54.4 Mg)/DAY [LINTERS]

Source: American Defense Preparedness Assoc. Wastewater Treatment in the Military Explosives and Propellants Industry. 3 Vols, Washington, D. C., Oct. 1975.

Table.22. GASEOUS EMISSIONS FROM NITROCELLULOSE MANUFACTURING PROCESSES

Source	Source Location	Exit Gas Flow Rate m^3/s	kg/Mg NC			Annual Prod. Gg
			SO_x	HNO_3 Mist	NO_x	
Nitrocellulose Mfg.[a]	Sunflower AAP	6.13	-	-	6	24.8[b]
Nitrocellulose Mfg.[a]	Sunflower AAP	-	-	-	6	30.4[b]
Nitrocellulose Mfg.	Radford AAP	8.89 @ 35°C	.45	-	20	32.7
Nitrocellulose Mfg.						
High Grade[c]	Badger AAP	2.16	-	-	3.0	19.4[b]
High Grade[c]	Badger AAP	2.62	-	-	2.1	19.4[b]
High Grade[c]	Badger AAP	2.42	-	-	1.9	19.4[b]
Low Grade[c]	Badger AAP	3.16	-	-	4.4	23.2[b]
Low Grade[c]	Badger AAP	2.77	-	-	2.4	26.8[b]
Nitrocellulose[a]	Sunflower AAP	1.79	-	-	4.3	8.28 (Dry)
Nitrocellulose						
Batch Lines A & B	Radford AAP	8.23	.47	25.7	21.0	31.3
Batch Line C	Radford AAP	4.54	.23	4.6	9.6	17.4
Nitrocellulose						
Batch Lines A & B[c]	Radford AAP	7.79	(50 ppm)	(3,000 mg/m³)	(1000 ppm)	-
Batch Line C[c]	Radford AAP	3.62	(10 ppm)	(30 mg/m³)	(530 ppm)	-
Boiling Tub	Radford AAP	0.033	-	-	(250 ppm)	-

[a]Equipped with a packed absorption column (85% removal of NO_x).

[b]Maximum design valve.

[c]Equipped with a water spray scrubber.

Source: Nelson, T. P. and R. E. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319, Task 50, July 1976.

7. References

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

2) Processes Research, Inc. Air Pollution from Nitration Processes. Contract No. CPA 70-1, Task 22. Cincinnati, Ohio, March 1972.

Purification

1. Function - Purification of nitrocellulose is an involved and tedious operation. The basic cellular structure of the parent material (cotton linters or wood pulp), which is retained on nitration, acts to entrap residual spent acids. Failure to remove the traces of spent acid renders NC unstable during storage.

Purification of the crude nitrocellulose takes place in a number of discrete steps, each taking place in a so-called "house," as follows:

- Boiling tub house - the NC/water slurry from the drowning tub is separated, and the water vehicle (approximately 3% total acidity) is discharged to the boiling tub pits. Sufficient water is added to the wet NC in the boiling tub to bring total acidity level to 0.25 to 0.50%. Steam is then passed through heating coils in the large wooden boiler tubs and the material is boiled for an extended period of time. This acid hydrolysis, or "sour boil," destroys unstable sulfate esters and nitrates of partially oxidized cellulose. After completion of the sour boil, water is drained to the boiling tub pits and the NC is washed with recovered or filtered water. The NC then is treated in two neutral boils using filtered water. The NC is washed with recovered or filtered water after each boil. Water from the two neutral boils and washes is discharged to the boiling tub pits. The NC is then slurried in water and pumped to the next purification step.

- Beater house - Dilute Na_2CO_3 is added to the NC slurry from the boiling tubs until the material is slightly alkaline. The material is then pumped through primary and secondary Jordan beaters, pulping devices similar to those used in the paper industry. Here the fibrous material is reduced to a physical state more amenable to purification. The operation is continued until the NC is reduced to the desired degree of fineness, as determined by settling tests. After settling and decantation of the alkaline water, the NC is transferred as a slurry to the next step.

- Poacher house - Sodium carbonate solution is added to the slurry from the beaters and the material is boiled. The soda ash treatment is followed by several fresh water (neutral) boils and a minimum of two washes with fresh water. The material is screened to remove unpulped fibers and separated by centrifugation. The centrifugate is discharged to the poacher settling pits and the NC precipitate is reslurried and pumped to the next operation.

- Blender house - In this step the NC is circulated as a water slurry and sampled for final product quality. At this stage NC fines known as "pit cotton" recovered from the settling pits are added when making up blends which contain both low-grade and high-grade nitrocellulose.

- Final wringer house - The NC slurry from the blender house is "wrung" by centrifugation to approximately 30% moisture content and then stored or processed in accordance with specific end-use requirements for the batch.

2. Input Materials - Nitrocellulose enters the purification process as a water slurry with a total acidity of approximately 3% and is transported as a slurry through the entire purification process. Soda ash (Na_2CO_3) is added to the slurry entering the beater house on the basis of 1 g Na_2CO_3/kg NC. In the poachers soda ash is added to the slurry on the basis of 4 to 5 g Na_2CO_3/kg NC. Process water requirements for purification are shown in Figure 8 in Process No. 7.

3. Operating Parameters - Residence time for NC in the boiling tubs varies according to the product being treated. Pyrocellulose and pyroxylin are subjected to 40 hours of boiling treatment that involves three changes of water. Guncotton is subjected to a sour boil for 60 hours, followed by two 5-hour neutral boils. Hydrolysis (sour boil) is performed at an acid content of 0.25 to 0.50%, calculated as H_2SO_4. In the poachers the NC slurry is subjected to a four-hour boil in soda ash solution, followed by a two-hour neutral boil in filtered water. According to information contained in one source, the NC may be subjected to two additional neutral boils of one-hour durations. The poached NC is then allowed to settle for up to one hour before separation and transport to the blender house. All boiling and poaching operations are carried out at 96°C. Specific data relating to batch size were not found in sources consulted for this study. However, from examination of known values for such parameters as 1) daily production level, 2) time for purification, and 3) batch size in the nitration process, it is evident that crude NC is pooled for purification and that large quantities of crude NC are purified in each batch.

4. Utilities - Figure 8, Process No. 7 shows the general product flow and water balance for a typical batch NC production line. Data on consumption of steam for heating the various purification boilers, of fuel used in steam production, or of other energy expenditures were not found in the sources consulted for this study.

5. Waste Streams - The extremely large volumes of process water associated with the manufacture of NC makes the treatment and disposal of waste water a formidable problem. Acidic wash waters and boiling tub washes drain to settling pits where NC fines are removed.

Overflow from the pits flows to waste acid neutralization facilities where $CaCO_3$ (as a lime slurry) is added to neutralize the acids present. After neutralization, the material is either discharged directly or transferred to settling lagoons. Approximately 13.6 x 10^6 kg $CaSO_4$ sludge is generated yearly as a result of waste acid neutralization at one NC production facility. The settling lagoons for this specific plant are drained at 3 to 6 month intervals and the sludge is removed for burial on adjacent land. The burial site is located on flat land and shows no visible signs of leaching.

Waste water from the beater, poacher and blender houses flows to another settling pit area where NC fines settle out. Effluent from the pit is either recycled to the wash lines or is discharged.

NC fines constitute a major portion of the total suspended solids in the waste water discharges of NC production facilities and can be expected to approximate the NC fines lost during the various processing steps. One source lists the following losses during NC purification:

Boiling tub house - 68.2 kg/day

Jordan beater house - 295 kg/day

Poacher house - 295 kg/day

A summary of overall waste water discharges as a result of NC production at two manufacturing facilities is shown in Table 23.

Possible sources of air emissions are the boiling tubs where steam and acid vapors are vented. The National Emission Data System emission factor for this process predicts 2.0 g NO_x/kg NC produced.

6. EPA Source Classification Code - Boiling tubs: 3-01-041-03

7. References -

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

2) Environmental Protection Agency, Mid-Atlantic Region, Report on Waste Disposal Practices, Radford Army Ammunition Plant, Radford, Virginia. Philadelphia, Pa., May 1973.

3) Explosives. In: Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 8. H. F. Mark, ed. N.Y., Wiley, 1966, pp. 581-718.

4) Processes Research, Inc. Air Pollution from Nitration Processes. Contract No. CPA 70-1, Task 22. Cincinnati, Ohio, March 1972.

Table 23. OVERALL DISCHARGES RESULTING FROM THE PRODUCTION OF NITROCELLULOSE AT TWO MILITARY FACILITIES

Parameter	Radford Army Ammunition Plant Discharge kg/day	Radford Army Ammunition Plant Discharge kg/Mg NC[a]	Badger Army Ammunition Plant Discharge kg/day	Badger Army Ammunition Plant Discharge kg/Mg NC[b]
$NO_2 + NO_3/N$	2,130-7,440	35.9-125	7,260	178
TKN	2.11-76.6	0.035-1.29	NA	NA
COD	4,290	72.0	5,440	134
BOD	13.1	0.221	NA	NA
Total Solids	630-112,000	10.6-1,890	109,000	2,665
Suspended Solids	761-1,960	12.8-33.0	8,250	202
Dissolved Solids	535-111,000	9.0-1,865	101,000	2,465
Volatile Solids	88.4-43,500	1.49-730	NA	NA
Acidity	0.798	.014	NA	NA
Alkalinity	31.7	0.535	NA	NA
TOC	1,550	26.1	1,380	33.9
NH_3-N	22.9	0.386	6.53	0.16
PO_4-P	1.72	0.029	17.1	0.42
Fe	NA	NA	26.0	0.64
SO_4	NA	NA	1,320	324

[a] 59.4 Mg/day NC produced
[b] 40.8 Mg/day NC produced
NA = Data not available

Source: Environmental Protection Agency, Effluent Guidelines Division. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Explosives Manufacturing Point Source Category. EPA 440/1-76-060-j, Group II. Washington, D.C., March 1976.

RDX/HMX Production Processes

Cyclotrimethylenetrinitramine or RDX is widely used as an ingredient of bursting charges and "plastic" explosives. This material, also known as Cyclonite, is currently replacing tetryl as a base charge in military detonators. RDX offers distinct logistical advantages over explosives dependent on petroleum derivatives as a base material. In addition, its stability is superior to that of PETN or tetryl and nearly equal to that of TNT.

The nitration reaction producing RDX results in low level contamination (<10%) with the related compound cyclotetramethylenetetranitramine (HMX). In its β-crystalline form HMX has little effect on the performance of RDX. By manipulation of reactant concentrations the reaction may be driven to HMX production. For this reason, RDX and HMX production processes are considered as one in this study.

Figure 9 is a flow chart for RDX/HMX production. Two processes are described: Nitration (Process No. 9) and Refinement (Process No. 10). RDX/HMX may be prepared by direct nitrolysis of hexamine or by interaction of formaldehyde, ammonium nitrate and acetic anhydride. The method described, a combination of these two methods, was originally developed during World War II. Refinement (Process No. 10) consists of nothing more than selective recrystallization from type-specific solvents.

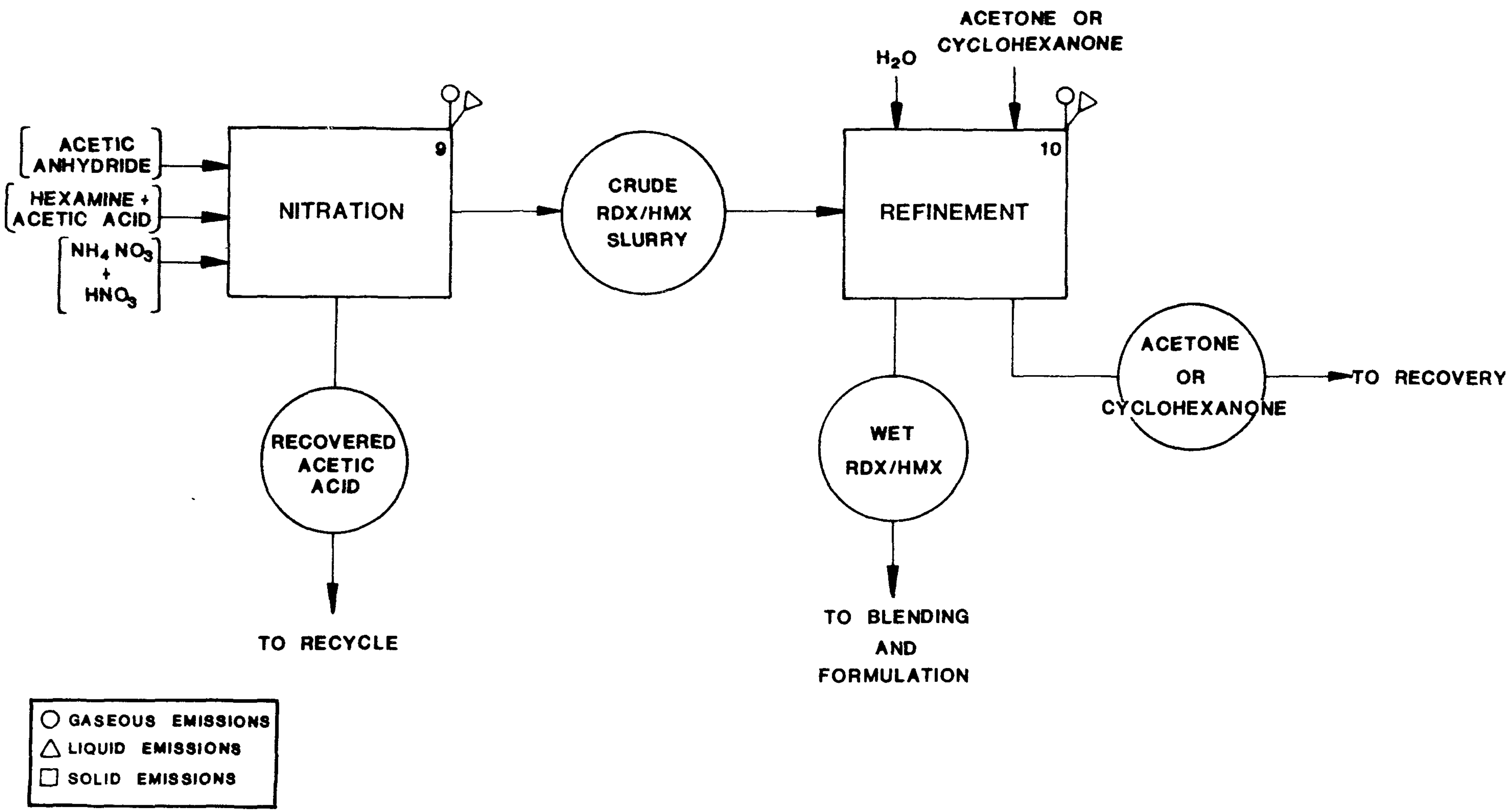
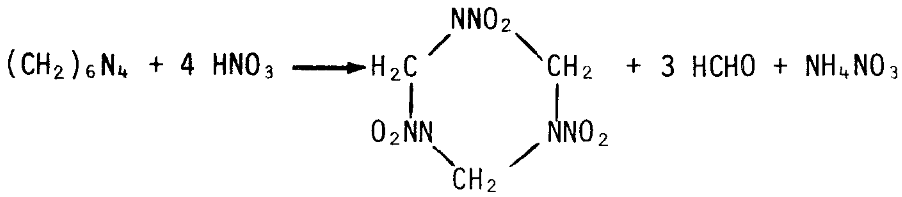


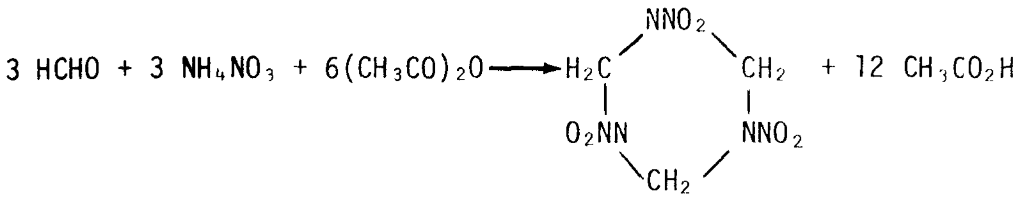
FIGURE 9. FLOW CHART FOR RDX/HMX PRODUCTION

Nitration

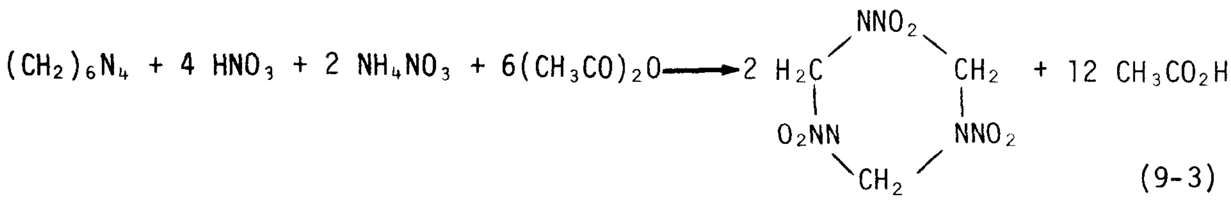
1. Function - The chemistry of RDX/HMX manufacture reveals a combination of two reactions. The first produces RDX by direct nitrolysis of hexamine and is ideally represented by:


(9-1)

The second, known as the Canadian reaction, produces RDX by the interaction of equivalent amounts of formaldehyde, ammonium nitrate and acetic anhydride according to the following scheme:


(9-2)

From the above it may be seen that the two by-products of direct nitrolysis are raw materials for the Canadian reaction. Since the nitrolysis reaction will occur under conditions favorable for the Canadian reaction, simple addition of reactions (1) and (2) yields:


(9-3)

A solution of hexamine in glacial acetic acid is introduced to the batch nitration vessel. Acetic anhydride is added, followed by a pre-mixed ammonium nitrate-nitric acid solution. The initial crude product contains RDX and HMX in varying proportions, according to reactant ratios as mentioned above. Various nitrated and acetylated derivatives of hexamine fragments contaminate the crude RDX/HMX.

After the nitration reaches completion, the reaction mixture is aged and simmered to hydrolyze the contaminating intermediates and then cooled to effect crystallization of crude RDX/HMX. Table 24 indicates the changes in composition of product as a result of the aging and simmering steps.

Table 24. EFFECT OF AGING AND SIMMERING ON COMPOSITION OF PRODUCT (RDX/HMX MANUFACTURE)

Reaction Products	Fresh Slurry		Aged Slurry		Simmered Slurry	
	kg[b]	%	kg[b]	%	kg[b]	%
RDX	20.61	79.48	22.57	84.78	22.57	91.08
HMX	1.59	6.13	1.66	6.73	2.21	8.92
BSX[a]	1.43	5.51	1.34	5.03	0	0
Other intermediates	2.30	8.87	1.05	3.94	0	0
Total	25.93	99.99	26.62	99.99	24.78	100.00

[a]BSX: Major reaction intermediate $(CH_3COOCH_2\text{-}N(NO_2)\text{-}CH_2)_2\text{-}N\text{-}NO_2$

[b]indicates kg of product from total batch weight of 100 kg of the following feed stream:
9.17 kg hexamine
14.97 kg acetic acid
30.57 kg ammonium nitrate/nitric acid
44.96 kg acetic anhydride
0.33 kg water

The crude RDX/HMX crystals are slurried in water and sent to a refining process. The filtrate from post-nitration filtration, along with the first wash water, is sent to a recovery facility where HNO_3 is neutralized with NaOH. The material is pumped to a primary evaporator where about 80 percent of its volume is volatilized and condensed as 60% acetic acid. The sludge remaining is diluted, heated to 100°C and seeded with RDX slurry. Additional RDX/HMX crystallizes as the mixture is cooled to 30°C. The explosive is recycled to the washing step of the line while the supernate is routed to a secondary evaporator for additional acetic acid recovery. The remaining sludge is steam stripped to recover residual acetic acid. All recovered acetic acid is purified, concentrated and recycled, and the stripped sludge enters the waste stream.

2. Input Materials - basis - 1.0 kg RDX produced

Input materials to this process consist of hexamine (0.406 kg) and acetic acid (0.633 kg), part of which is used as a solvent for the hexamine. Acetic anhydride (1.992 kg) and a premixed nitric acid/ammonium nitrate (1.354 kg) solution make up the balance of the feed stream.

Table 25 illustrates the different proportions of reactants used in making RDX and HMX.

Table 25. A COMPARISON OF REACTANT WEIGHT PROPORTIONS FOR RDX AND HMX PRODUCTION

Reactant	RDX Production (%)	HMX Production (%)
Hexamine	9.2	17.0
Acetic Acid	15.0	18.0
NH_4NO_3 - HNO_3	30.8	11.0
Acetic Anhydride	45.0	54.0

3. Operating Parameters - The ingredients are charged to the reactor at 75°C, which temperature is maintained during nitration and aging steps by circulating water through heat exchange coils in the reactor. Temperatures for simmering or first crystallization were not specified, nor were residence times for the reactants in any stage of this process.

4. Utilities - Specific data relating to consumption of utilities were not found in the sources consulted for this study.

5. Waste Streams - The reactor vessel, aging tank and simmer tank are vented to a scrubber where acid vapors are recovered and recycled as dilution liquor for the simmering step. Atmospheric emissions from the scrubber vents include NO_x, acetic acid, and traces of formic acid and methyl nitrate. Data for NO_x emission during RDX/HMX production are presented in Table 26.

The stripped sludge from acetic acid recovery is treated with NaOH, converting the ammonium nitrate to sodium nitrate and ammonia; any residual acetic acid to sodium acetate; and any residual RDX and HMX to ammonia, formates, amines and sodium nitrate. Small amounts of ammonia vent to the atmosphere as the vaporized ammonia is condensed. The condensate contains traces of impurities such as methylamine and dimethylamine which preclude its reuse in the nitration process. It is, however, generally disposed of for use as fertilizer, along with sludge residue, consisting mainly of sodium nitrate. Small amounts of ammonia and amines are discharged in the effluent waste-water.

Examination of Table 27 reveals that overall waste-water discharges from the RDX/HMX nitratation process (which, for the purpose of this study, includes

Table 26. GASEOUS EMISSIONS FROM RDX/HMX PRODUCTION PROCESSES

Source	Source Location	Exit Gas Flow Rate (m^3/s)	Emission Unit	kg/unit Acid Mist	kg/unit NO_x	Annual Prod. (Gg)
RDX Production	Holston AAP	Small	Mg of RDX	--	6.9	40.8
HMX Production	Holston AAP	Small	Mg of HMX	--	6.9	--
Condenser Vent on Acetic Acid Concentrator	Holston AAP	0.013	Mg of Acetic Acid	--	(490 ppm)[a]	48.3
Barometric Seal Exhaust-Acetic Anhydride Prod.	Holston AAP	0.084	Mg of Acetic Anhydride	(0.15 mg/m^3)[b]	--	46.4

[a]This effluent is 6.98% by volume hydrocarbons which include 0.051% methane by volume and 3.53% methyl formate, 2.93% methyl acetate, 18.17% methyl nitrate, 11.55% propyl formate, 1.15% propyl acetate, and 1.68% n-propanol by weight.

[b]Also contains 11.73% by volume of methane and 25.91% by volume non-methane.

Source: Nelson, T.P. and R. E. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319, Task 50, July, 1976.

Table 27. TYPICAL WASTE WATERS GENERATED BY RDX/HMX PRODUCTION

	Operation	Process Water[a]		Cooling Water		Total Water		BOD		COD		RDX		HMX		Acetic Acid		Cyclo-Hexanone	
		m^3/day	m^3/Mg	m^3/day	m^3/Mg	m^3/day	m^3/Mg	kg/day	kg/Mg	kg/day	kg/Mg	kg/day	kg/Gg	kg/day	kg/Gg	kg/day	kg/Gg	kg/day	kg/Gg
RDX[b]	Nitration	568	3.77	5,370	35.7	5,940	39.5	5,090	3.62	653	4.28	1.19	7.7	0.48	3	90.7	595	-	-
	Filter/Wash	723	20.9	-	-	723	20.9	0.93	0.62	0.47	0.032	4.36	29	0.27	2	232	1,540	-	-
	Recrystallize	416	2.77	92,000	613	92,400	616	370	2.46	192	1.28	NA	NA	NA	NA	NA	NA	88.9	590
	Dewater	563	3.88	-	-	583	3.88	1,600	10.6	2,480	16.5	28.5	189	0.87	6	NA	NA	82.5	545
HMX[c]	Nitration	71.2	29.8	6,550	2,740	6,990	2,770	NA	NA	10.0	4.2	NA	NA	NA	NA	NA	NA	-	-
	Filter/Wash	35.0	15.1	-	-	35.0	15.1	662	277	1,480	620	0.63	262	0.41	171	66.2	27,800	-	-
	Recrystallize	515	NA	NA	NA	NA	NA	171	NA	637	NA	4.99	NA	5.44	NA	NA	NA	302	NA
	Dewater	348	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

[a]Data does not include process water recycled for recovery of contaminants.
[b]0.150 Gg/day RDX produced.
[c]2.39 Mg/day HMX produced.

NA indicates data not available

Source: American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

filtration and washing of the crude RDX/HMX crystals) total approximately 9900 m^3 during a typical production day. In general process effluents containing substantial amounts of product, by-product or spent reactants are recycled for recovery of the material. Only relatively uncontaminated process water, cooling and pump seal water, and floor washings are discharged as waste water, first to catch basins and then to sewers.

Table 28 gives some indication of the effectiveness of catch basins in reducing the pollutant level in the effluent from RDX/HMX production. The current practice for disposal of materials recovered from catch basins is open burning.

6. EPA Source Classification Code - None exists for this process.

7. References -

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

2) Booz-Allen Applied Research, Inc. A Study of Hazardous Waste Materials, Hazardous Effects and Disposal Methods. 3 Vols. Vol. II, PB 221-466, Bethesda, Md., 1973.

3) U. S. Office of Scientific Research and Development, National Defense Research Committee, Div. 8. The Preparation and Testing of Explosives. Summary Technical Report of Division 8, NDRC. Washington, D. C., 1946, pp. 6-12.

Table 28. POLLUTANT DISCHARGES FROM RDX/HMX MANUFACTURE

	Production Source	Catch Basin Influent (I) or Effluent (E)	Wastewater Volume, m^3/d	Concentration, g/m^3 BOD	RDX	HMX
RDX	Nitration Reactor	I	188	2359	5.06	2.17
		E	188	2116	2.31	0.96
	Filtration and Washing	I	52.4	582	4.15	1.87
		E	52.4	1163	3.53	0.00
	Recrystallization	I	103	896	0.0	0.0
		E	103	339	0.0	0.0
	Dewatering	I	1,312	2771	49	1.5
		E	1,312	3229	33	0.7
HMX	Nitration Reactor	I	71.2	2393	0.0	0.0
		E	71.2	1840	0.0	0.0
	Filtration and Washing	I	-	5183	70.1	45.7
		E	-	6098	6.1	12.2
	Recrystallization	I	514	331	5.2	10.6
		E	514	322	5.2	4.4
	Dewatering	I	-	394	21.5	34.5
		E	-	375	20.9	9.2

Source: American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975

Refinement

1. Function - An organic solvent (cyclohexanone or acetone, depending on the desired product) is added to the RDX/HMX slurry received from the nitration process. The RDX/HMX crystals dissolve in the organic solvent and the solution is distilled. The residual solvent, supersaturated with RDX/HMX, is allowed to cool, and the explosive recrystallizes. The recrystallized RDX/HMX is filtered out and reslurried in water. The slurry is dewatered to approximately 10% H_2O prior to formulation in compound explosives.

2. Input Materials - RDX/HMX enters the process as a water slurry from Process No. 9. The solvent used for recrystallization may be acetone (for HMX production) or cyclohexanone (RDX) in quantities not specified. Process water makes up the balance of the feed stream to this process.

Specific data relating to quantities of the above materials in the feed stream for this process were not found in sources consulted for this study.

3. Operating Parameters - Specific data relating to temperature for distillation or recrystallization were not found in sources consulted for this study.

4. Utilities - Data were not found in sources consulted for this study.

5. Waste Streams - Some fugitive atmospheric emissions of vapors from the organic solvent distillation step may be expected. The major waste-water source from RDX/HMX refinement is cooling water from the recrystallization step. An examination of Table 27 (see Process No. 9) reveals that overall waste-water discharges for refinement of RDX, which include recrystallization and subsequent dewatering, total approximately 9300 m^3 during a typical production day. Of this total less than one percent is process water. Table 27 also shows the relative presence of various contaminants of the waste-water stream, while Table No. 28 (see Process No. 9) gives an indication of the effectiveness of catch basins in reducing pollutant levels in discharged sewage.

6. EPA Source Classification Code - None exists for this process.

7. References -

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

2) Booz-Allen Applied Research, Inc. A Study of Hazardous Waste Materials, Hazardous Effects and Disposal Methods. 3 Vols. Vol. II, PB 221-466, Bethesda, Md., 1973.

3) U. S. Office of Scientific Research and Development, National Defense Research Committee, Div. 8. The Preparation and Testing of Explosives. Summary technical report of Division 8, NDRC. Washington, D.C., 1946.

Nitroglycerin (NG) Production Processes

Nitroglycerin is commonly manufactured by two processes. Commercial production generally takes place using the older "batch" method while most military production utilizes a continuous flow process. Figure 10 presents a flow chart illustrative of either production method. Differences between the two methods are mechanical rather than chemical in nature. Greater volumes of reactant and/or product are present at any particular stage during batch processing, but relative concentrations and operational sequences are similar to those found in continuous flow production.

Two military production plants have "batch" NG lines, but one is not in present use, and the second is scheduled for replacement by the continuous process. Once replacement is accomplished, all NG manufactured at military facilities will be produced by the Biazzi continuous flow method. Review of processes at a number of commercial NG production facilities also indicates a general trend toward conversion to the continuous process.

The Biazzi process for continuous nitration of glycerin is one of the safest methods known for the production of this highly unstable explosive compound. Like all continuous processes, the Biazzi method is characterized by a very small inventory of raw nitroglycerin at any stage in the production line and by careful balancing of flow rates and cooling. Despite the small quantities present at any one time, a typical plant in continuous operation can produce 1000 kg/hr.

Spent acid recovery systems and their resultant waste streams are virtually identical for batch and continuous methods. As shown in Table 29, waste waters generated by batch and continuous flow production are markedly similiar. For these reasons, and because it is expected that the bulk of NG produced in the future will result from continuous flow processes, a detailed description of batch production methods will not be made in this report.

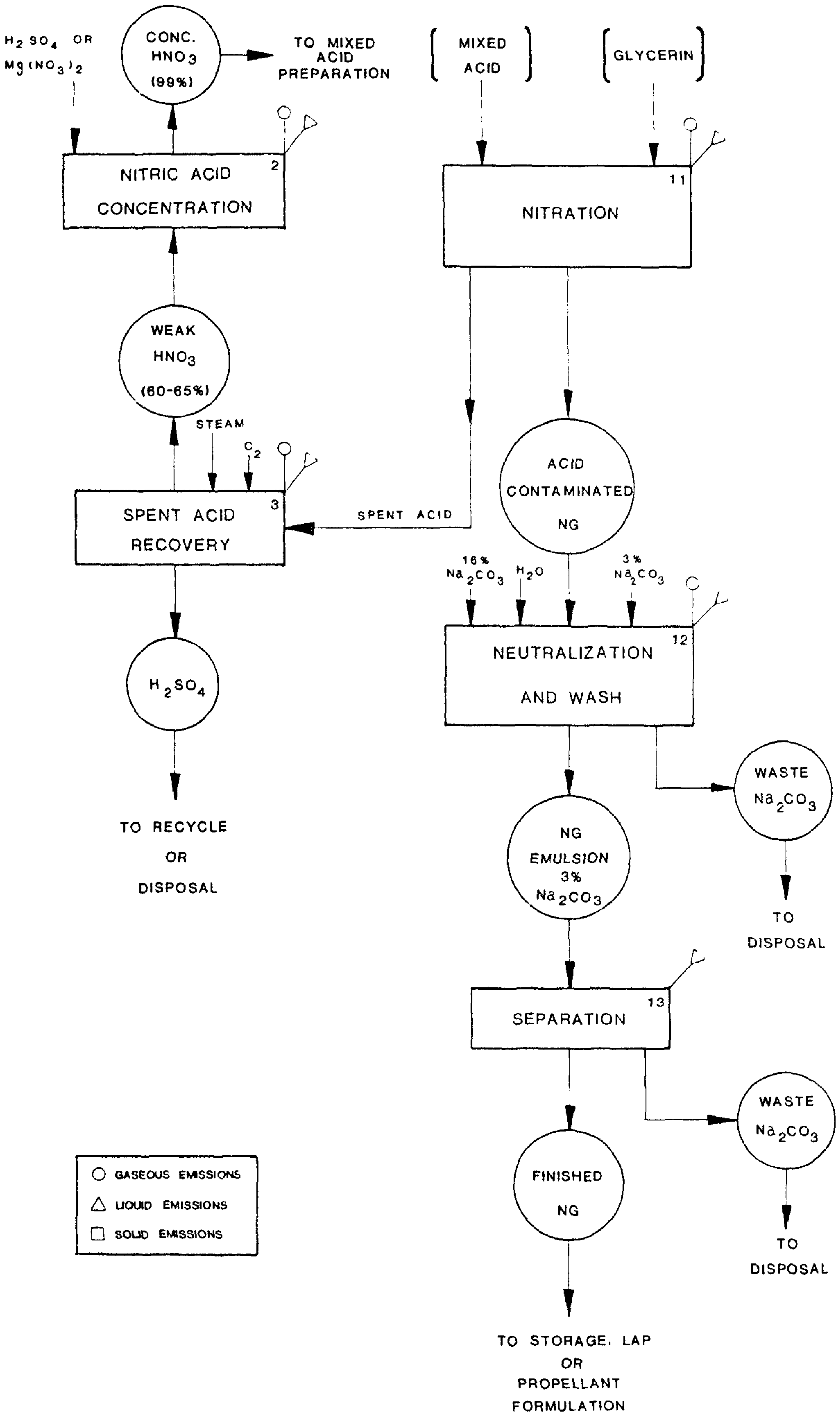


FIGURE 10 FLOW CHART FOR NITROGLYCERIN PRODUCTION

Table 29. AVERAGE WASTE WATER CHARACTERISTICS OF NITROGLYCERIN PRODUCTION

	Biazzi Process		Batch Process	
Parameter[a]	Military Nitration and Acid Recovery Waste Water	NG Storage Waste Water	Military Total Waste Water	Commercial Total Waste Water
Flow, m^3/d	56.775	18.925	416.35	36.714
pH	8.6	10.5	4.7	2.7-10.0
Temp. °C.	NA	NA	14.6	-
BOD	4.5	3.2	NA	NA
COD	1228	912	109.1	2260
Kjeldahl - N	NA	NA	2.5	23.0
Nitrate - N	13280	477	116.6	5564
Sulfate	1416	130	242.6	3154
Susp. Solids	23.0	11.3	NA	NA
Dissol. Solids	81626	13905	NA	NA
Nitroglycerin	1300	266	NA	315-12700
Dinitroglycerin	850	130	NA	NA

[a]Parameter values in g/m^3 unless otherwise indicated

NA indicates data not available in sources consulted for this study.

Source: American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

Nitration

1. Function - Chemically, nitroglycerin is glyceryl trinitrate and is prepared by the nitration of glycerin with mixed nitric and sulfuric acids according to the following idealized equation:

$$\begin{array}{ccccccccccccccccc} & H & & H & & H & & & & H & & H & & H & & \\ & | & & | & & | & & & & | & & | & & | & & \\ H - & C & - & C & - & C & - H + 3\,HNO_3 & \xrightarrow[2\text{-}25^\circ C]{H_2SO_4} & H - & C & - & C & - & C & - H + 3\,H_2O & (11\text{-}1) \\ & | & & | & & | & & & & | & & | & & | & & \\ & OH & & OH & & OH & & & & NO_3 & & NO_3 & & NO_3 & & \end{array}$$

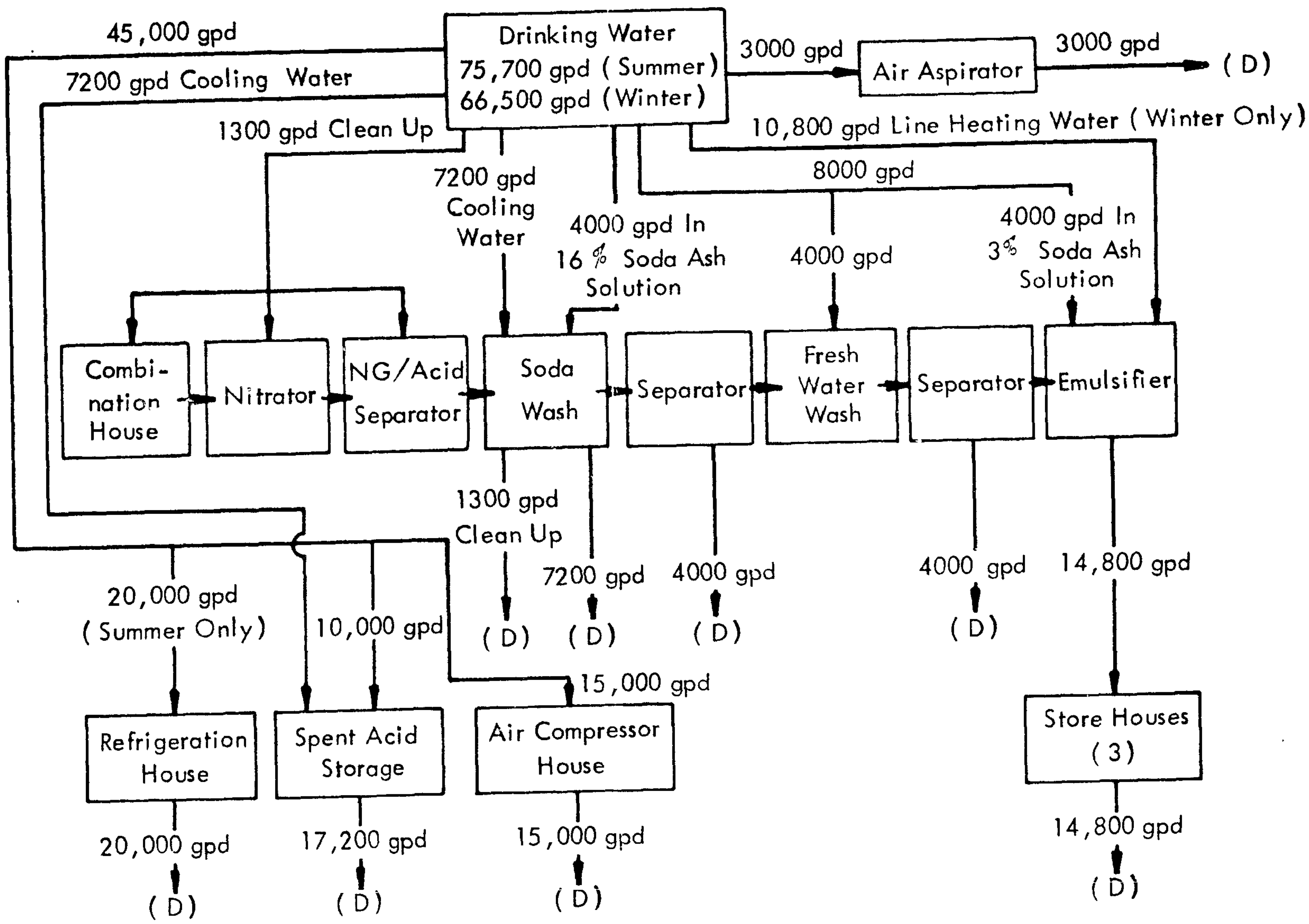
Sulfuric acid catalyzes the reaction by forming a hydrated molecule with the water of reaction, thus shifting reaction equilibrium to the right.

Mixed acid and glycerin are metered into and through the nitration vessel. Cooling of the reactor is accomplished by circulation of brine through heat exchange coils contained therein. Glycerin flow is regulated with a proportioning pump and is supplied at a rate dependent on the strength of the nitrating acid. The effluent from the nitrator, consisting of nitroglycerin and spent acid, is separated by continuous flow centrifugation. The spent-acids flow to a recovery unit for treatment and the raw (acid contaminated) nitroglycerin proceeds to neutralization and washing.

2. Input Materials - Basis - 1.0 kg NG. The feed stream to this process consists of glycerin (0.422 kg) and a mixed acid containing 0.868 kg HNO_3 and 0.826 kg H_2SO_4. The H_2SO_4 is prepared by mixing 60% oleum with 93% H_2SO_4 to produce a 40% oleum. This mixture is then mixed with 97% HNO_3 to give the desired concentrations. Process yield is about 96% of theoretical.

3. Operating Parameters - The continuous flow nitration vessel has a capacity of about 120 liters. It is uninsulated and is equipped with an agitator and internal heat exchange coils for cooling. A 15 cm opening in the bottom with a quick release valve allows emergency drowning of the reactor contents. The mixed acid is fed to the surface of the reactor charge while glycerin is fed below the surface. Temperature is controlled at about 15°C; pressure is atmospheric.

4. Utilities - See Figure 11 for water balance for typical Biazzi NG production line. Water consumption during the nitration process is approximately 4.92 m^3/day at 2400 kg/day NG production rate or 2.05×10^{-4} m^3/kg nitroglycerin produced. This water is used primarily for equipment and floor wash down. Data relating to consumption of other utilities were not found in sources consulted for this study.



(D) - Discharge to Sewer (Total - 86,500 gpd)

M^3/S = gpd (4.38×10^{-8})

Figure 11. WATER BALANCE FOR TYPICAL BIAZZI NG PRODUCTION LINE (24,000 kg/day output)

Source: American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols Washington, D.C., Oct. 1975.

5. Waste Stream - The nitration reactor is vented through an absorber to the atmosphere. Emissions include NO_x and HNO_3 fumes in unknown quantities. Typical NO_x emission is estimated at 0.3 g/kg product. Specific levels of waterborne pollutants are not specified for this process. Waste waters emanate solely from building and equipment cleanup operations and can be expected to contain minimal amounts of pollutants. The process for recovery of spent acid from nitration of glycerin is identical with that for the recovery of other spent nitration acids. For a full description refer to Process No. 3. A summation of combined waste-water discharge from nitration and spent acid recovery processes in NG production was shown previously in Table 29.

6. EPA Source Classification Code - None exists for this process.

7. References -

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

2) Processes Research, Inc. Air Pollution from Nitration Processes. Contract No. CPA 70-1, Task 22. Cincinnati, Ohio, March 1972.

Neutralization and Wash

1. Function - Raw (acid-contaminated) nitroglycerin is neutralized by countercurrent washing in three successive soda ash baths. The effluent from the third wash is separated by continuous flow centrifugation. The spent soda ash solution flows to catch basins, and the neutralized NG flows to a double fresh water wash. Another centrifugation follows the water wash, after which the NG is reemulsified in a weak soda ash solution and transferred to temporary storage. The wash water flows to catch basins for ultimate disposal.

2. Input Materials - Soda ash solutions used for acid neutralization contain 16% Na_2CO_3. The soda ash solution used for final emulsification of neutralized and washed NG contains 3% Na_2CO_3. Consumption rate for 16% Na_2CO_3 solution, fresh water and 3% Na_2CO_3 solution is 0.6308 ℓ of each /kg NG. On a full production basis with daily output of NG standing at 24,000 kg, approximately 15.14 m^3/day of each reagent is consumed.

3. Operating Parameters - Data relating to operating temperature and pressure were not found in sources consulted for this study. Flow rates for the reagents at 24,000 kg/day production may be determined from water balance data presented in Figure 11 (see Process No. 11). Cooling water is supplied to the 16% soda ash washers at a rate of 27.25 m^3/d during maximum productions.

4. Utilities - See Figure 11 for water balance for a typical Biazzi NG production line. Water consumption stands at 72.6 to 113.6 m^3/day. Of this, 41 m^3 is line heating water, used only during winter months. Process water amounts to 45.4 m^3/day while cooling water during acid neutralization accounts for the balance of 27.2 m^3/day. The above figures are valid for a production of 24,000 kg NG/day. Specific data relating to consumption of other utilities were not found in sources consulted for this study.

5. Waste Streams - The washers are vented to the same absorber as the nitrator and emissions are considered as part of the nitration process. Wastes from neutralization and wash account for the bulk of waste loading contained in effluent waters described in Table 29 under Nitration and Acid Recovery Waste Water.

6. EPA Source Classification Code - None exists for this process.

7. References -

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

2) Processes Research, Inc. Air Pollution from Nitration Processes. Contract No. CPA 70-1, Task 22. Cincinnati, Ohio, March 1972.

Separation

1. Function - Upon withdrawal from temporary storage, NG is separated from the vehicle of 3% Na_2CO_3. The weak soda ash solution is drained to catch tanks where any suspended NG settles out for recovery. NG from the separator is desiccated and transported to storage magazines or to a production area for subsequent formulation into explosive or propellant mixtures.

2. Input Materials - An emulsion of NG in 3% Na_2CO_3 constitutes the feed stream to the process.

3. Operating Parameters - Specific data relating to operating parameters for the process were not found in sources consulted for this study.

4. Utilities - No information was found in sources consulted for this study.

5. Waste Streams - The only significant waste stream generated by this process stems from separation and disposal of the 3% Na_2CO_3 vehicle. Specific contaminants found in waste water from separation of the NG/soda ash emulsion are shown in Table 29.

6. EPS Source Classification Code - None exists for this process.

7. References -

1) American Defense Preparedness Assn. Wastewater Treatment in the Military Explosives and Propellants Production Industry. 3 Vols. Washington, D.C., Oct. 1975.

2) Processes Research, Inc. Air Pollution from Nitration Processes. Contract No. CPA 70-1, Task 22. Cincinnati, Ohio, March 1972.

Pentaerythritol Tetranitrate (PETN) Production Processes

Pentaerythritol tetranitrate (PETN) is produced by nitration of pentaerythritol. Unlike other organic nitrates, PETN is manufactured on a commercial scale by the use of nitric acid rather than a mixture of nitric and sulfuric acids.

Data for utilities consumed and waste streams generated during production of this material are generally unavailable. A comparison with similar processes indicates that certain characteristic waste products are to be expected, as stated in the individual process descriptions.

Figure 12 is a flow sheet for the processes that follow. The processing sequence presented here, consisting of Nitration (Process No. 14) and Stabilization (Process No. 15), is considered typical of production in general and thus is representative of batch, semicontinuous, or continuous production techniques.

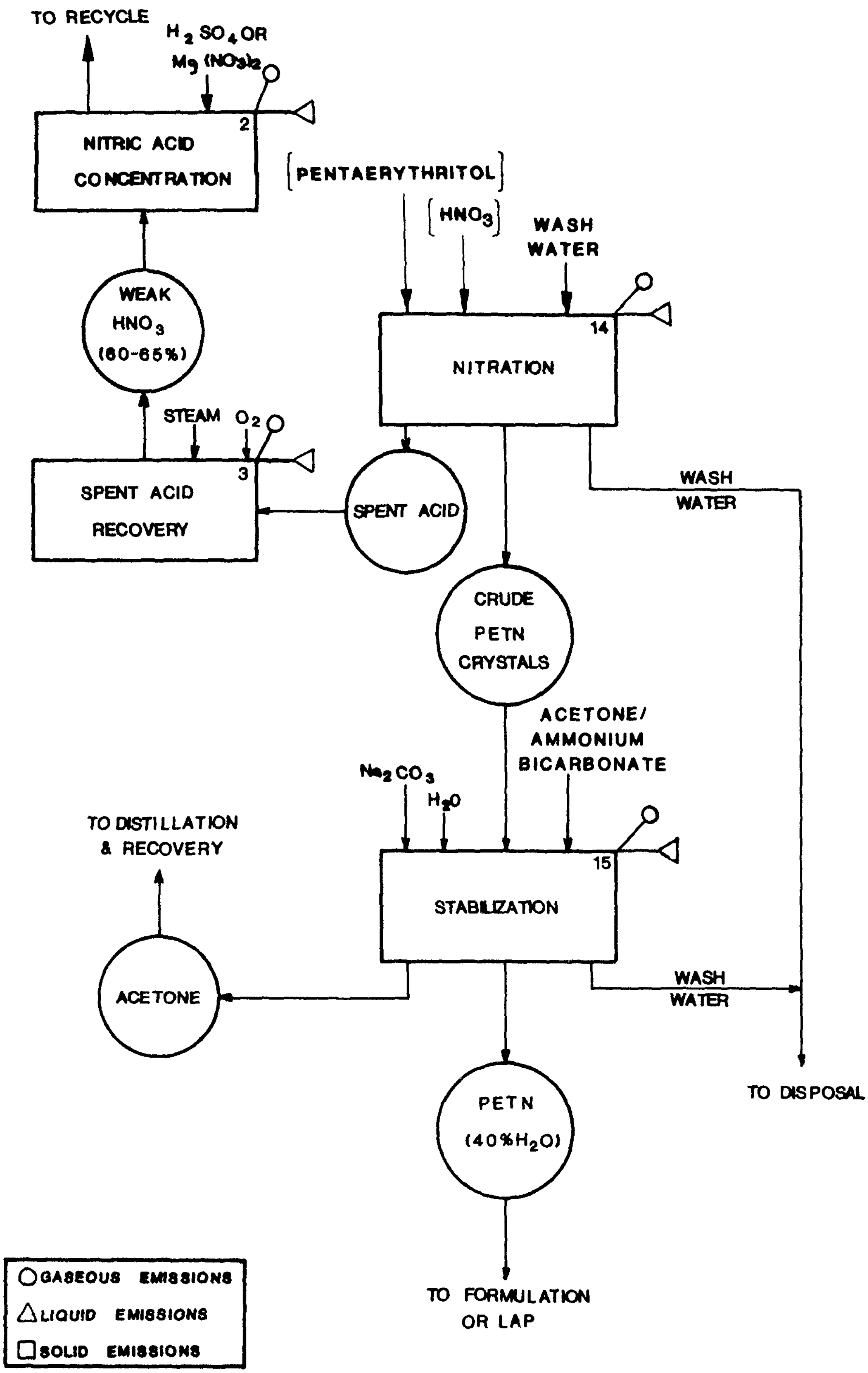


FIGURE 12. FLOW CHART FOR PETN PRODUCTION

Nitration

1. Function - Pentaerythritol (PE) is reacted with concentrated nitric acid in a water-cooled reactor, forming crystals of the tetranitrate. This reaction is represented by the following:

$$\begin{array}{c} CH_2OH \\ | \\ HOH_2C-C-CH_2OH \\ | \\ CH_2OH \end{array} + 4\ HNO_3 \xrightarrow[20^\circ C-23^\circ C]{} \begin{array}{c} CH_2ONO_2 \\ | \\ O_2NOH_2C-C-CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array} + 4\ H_2O \qquad (14\text{-}1)$$

The crystals so formed are separated from spent acid by centrifugation or filtration and water washed to remove residual acid. Spent acid from the nitration process goes to recovery. PETN crystals from the water wash are further refined in the stabilization process.

2. Input Materials - Basis - 1.0 kg PETN. PE (0.462 kg) and nitric acid (0.857 kg) are the sole constituents of the feed stream to this process. The yield of PETN is approximately 93 percent of theoretical.

3. Operating Parameters - During batch nitration, initial acid temperature in the water-cooled reactor is 18°C. PE is added at a rate sufficient to elevate and maintain reaction temperature at 22°C to 23°C. After addition of PE is completed, the reaction mixture is stirred and cooled for an additional 20 minutes. Specific data for temperature control or flow rates during continuous or semicontinuous operation were not found in sources consulted for this study.

4. Utilities - Data relating to utilities consumption were not found in sources consulted for this study.

5. Waste Streams - Data relating to specific gaseous or liquid wastes from the nitration process were not found in sources consulted for this study. Waste streams for recovery and concentration of spent HNO_3 should be similar to those for HNO_3 spent acid recovery (see Process No. 3) from production of other explosives. Effluent from the first water wash becomes part of the waste stream but no indication is made of any treatment prior to disposition as waste water.

6. EPA Source Classification Code - None exists for this process.

7. References -

1) Davis, Tenney L. The Chemistry of Powder and Explosives. N.Y., Wiley, 1941, 1943.

2) Explosives. In: Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 8. H. F. Mark, ed. N.Y., Wiley, 1966, pp. 581-718.

3) Hedley, W. H., et al. Potential Pollutants from Petrochemical Processes, final report. Contract 68-02-0226, Task 9, MRC-DA-406. Dayton, Ohio, Monsanto Research Corp., Dayton Lab., Dec. 1973.

4) U.S. Office of Scientific Research and Development, National Defense Research Committee, Div. 8. The Preparation and Testing of Explosives. Summary Technical Report of Division 8, NDRC. Washington, D.C., 1946.

Stabilization

1. Function - PETN crystals, water washed after separation from the nitrating acid, are suspended in a dilute Na_2CO_3 solution to neutralize residual acid. The slurry is then filtered and the crystalline explosive is washed with water. The washed PETN crystals are then dissolved in hot acetone containing a small quantity of ammonium bicarbonate. The solution is filtered and PETN recrystallized (or grained) by the addition of water. The PETN crystals are filtered from the acetone/water/ammonium bicarbonate milieu and water washed to remove traces of acetone. The acetone/water filtrate is digested with NaOH (pH 10) to destroy any contaminating explosive and the acetone is recovered by distillation. Still bottoms are discharged as part of the waste-water stream. The wet PETN (40% H_2O) is considered the final product and is generally not dried before being used in the production of formulated explosives or specific hardware items.

2. Input Materials - Wet PETN crystals from Process No. 14 constitute the primary feed stream to this process. Sodium carbonate, acetone, and ammonium bicarbonate in unspecified quantities are used as reagents for stabilization of the crude PETN. Water acts as a vehicle for slurrying and as a washing agent.

3. Operating Parameters - Acetone at 50°C is used for dissolution of PETN crystals. No other operating temperatures are specified, nor are any other operating parameters, e.g., Na_2CO_3 or $(NH_4)HCO_3$ concentrations, acetone/water ratio for recrystallization.

4. Utilities - No data were specified in sources consulted for this study.

5. Waste Streams - No data were found specifying volume or quality of waste waters or gaseous emissions from this process. It is to be expected that waste waters will be contaminated with traces of the basic salts used for stabilization of PETN as well as nitrates formed by reaction of these basic salts with residual nitric acid. In addition the waste stream may contain traces of acetone.

Emissions of acetone vapors may be encountered as fugitive gaseous emissions from the distillation equipment in the acetone recovery system.

6. EPA Source Classification Code - None exists for this process.

7. References -

1) Environmental Protection Agency. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Explosives Manufacturing Point Source Category. EPA 440/1-76/060-j, Group II. Washington, D.C., March 1976.

2) Hedley, H. W., et al. Potential Pollutants from Petrochemical Processes, final report. Contract 68-02-0226, Task 9, MRC-DA-406. Dayton, Ohio, Monsanto Research Corp., Dayton Lab., Dec. 1973.

3) U.S. Office of Scientific Research and Development, National Defense Research Committee, Div. 8. The Preparation and Testing of Explosives. Summary technical report of Division 8, NDRC. Washington, D.C., 1946.

APPENDIX A

RAW MATERIALS

Table A-1. RAW MATERIALS FOR NITRATION PROCESSES

ammonia
magnesium nitrate
sulfur
acetic acid
sodium carbonate
ammonium bicarbonate
acetone
cyclohexanone
sodium sulfite
water
calcium carbonate
sodium hydroxide
toluene
cellulose - cotton linters or specially prepared wood pulp
hexamine
ammonium nitrate
gylcerine
pentaerythritol

Table A-2. INGREDIENTS ADDED TO NITRATED ORGANIC COMPOUNDS IN FORMULATED PRODUCTS

aluminum
ammonium perchlorate
calcium chloride
nitroguanidine
ammonium nitrate
ammonium picrate
polybutadiene
polyurethane
wax
sodium nitrate
polymeric binder
sodium chloride
sulfur
phenolic resin beads
bagasse
sawdust
wood flour
coal
corn meal
corn starch
grain and seed hulls and flours
trace inorganic salts
guar gum
gelling agents
fumaric acid
ethylene glycol
ammonium sulfamate
fuel oil
atticote
ferrophosphate
calcium silicate
mineral oils and jelly
azides
fulminate of mercury
picric acid
centralites
diphenylamine
diphenylurethane, ethyl N,-N'-diphenylcarbamate
ethyl N-phenylcarbamate
2-nitrodiphenylamine
phthalate esters
triacetin
ether

Table A-2. INGREDIENTS ADDED TO NITRATED ORGANIC COMPOUNDS IN FORMULATED PRODUCTS (Continued)

acetone
ethyl alcohol
graphite
carbon black
ammonium chlorate
potassium nitrate
barium nitrate
potassium sulfate
potassium chlorate
poly (methyl acrylate)
polyisobutylene
polystyrene
poly(vinyl chloride)
adipates
sebacates

APPENDIX B

PRODUCTS

Table B-1. CHARACTERISTICS AND USES OF THE MORE IMPORTANT PRIMARY HIGH EXPLOSIVES

Name	*Composition or Chemical Formula*	*Density g/cc*	*Detonation Velocity[a] (km/sec)*	*Detonation Pressure (kilobars)*	*Detonation Temperature[a] (°K)*	*Sensitivity*	*Major Characteristics*	*Uses*
Mercury fulminate	$Hg(ONC)_2$	3.6	4.7	220	6900	Very high	Best primary explosive for single-component (fuse) detonators, easily detonated by flame, spark, heat, or friction; easily dead-pressed.	In fuse caps (mixed with $KClO_3$), propellant primer, in fuses for shells; small arms cartridge caps.
Lead azide	PbN_6	4.0	5.1	250	5600	Very high (higher than NG less than mercury fulminate)	Powerful detonator but requires strong igniters, e.g., lead styphnate.	Primary explosive in composition (EB) caps; military fuses.
Lead styphnate	$C_6H(NO_2)_3O_2Pb$	2.5	4.8	150	-	Exceedingly high	Extremely sensitive to sparks, static electricity, explodes rapidly on ignition; good thermal stability.	Igniter in composition caps, military fuses; very satisfactory detonator explosive for fast ignition.
Nitromannite (Mannitol hexanitrate)	$C_6H_8(ONO_2)_6$	1.73	8.3	300	6000	Very high (greater than NG, less than lead azide)	Stronger and more brisant than NG, RDX, PETN.	In composition caps and fuses.
Dinitrodiazophenol (DDNP)	$C_6H_2N_4O_5$	1.5	6.6	160	--	Very high (less than lead azide)	Does not dead-press. About 3/4 as strong as TNT.	In composition caps and fuses.

[a]Most important properties of detonators.

"Reprinted from Reigel's Handbook of Industrial Chemistry, 7th Ed
James A. Kent, ed. Van Nostrand Reinhold, 1974.

Table B-2. CHARACTERISTICS AND USES OF THE MORE IMPORTANT SECONDARY HIGH EXPLOSIVES

Name	*Composition or Chemical Formula*	*Density (g/cc)*	*Detonation Velocity (km/sec)*	*[illegible] Energy (kcal/g)*	*Sensitivity*	*Major Characteristics*	*Uses*
Ammonia gelatin dynamites	30–90% grades same as straight gelatins except for some NG and $NaNO_3$ replacement by NH_4NO_3	1.2–1.5	4–6.5	0.75–1.35	High	More economical, only slightly less brisant than straight gelatin, exhibits low-order detonation with threshold priming and high pressures.	General small and large diameter blasting in hard rock and under water
Semigelatin dynamite	15–20% NG, 1–2% DNT oil, AN-SN dope	1.2	3.5–5 (depends on diameter)	0.9	High	Stringy, plastic; easily loaded in "uppers;" economical, high strength, moderate brisance	Popular small diameter metal-mining explosive.
Prilled AN-Fuel Oil	94/6 NH_4NO_3/oil	0.8–0.9	1.5–4	0.81–0.83	Low (requires booster)	One of the cheapest sources of explosive energy available today, flammable and will explode when ignited under strong confinement; no water resistance, adaptable to do-it-yourself operations	Open-pit and underground blasting where dry conditions prevail, most adaptable to soft, easy shooting.
Slurry explosives TNT-SE	TNT 17–40 Oxidizer* 30–65 H_2O 12–25 Al 0–20 Other 0.3–1.5	1.4–2.0	5–8	0.7–1.8	Low (requires boosters)	Gel or thick pea-soup consistency, capable of detonation at high pressures, excellent water resistance.	Large diameter, open-pit, small diameter underground, oil well, submarine, water-filled boreholes, deep-water bombs.
Smokeless powder SE	SP 20–40 Oxidizer* 30–60 H_2O 3–25 Al 0–20 Other 0.3–10	1.35–1.9	4–7	0.65–1.[illegible]	Low (requires boosters	Generally similar to TNT slurry	Large diameters, open-pit blasting.
Al-SE	Al 1.0–10	1.1–1.5	2–5	0.7–1.3	From cap sensitive to very low depends on aluminum fineness	Gelatin; no explosive ingredients.	Small diameter, underground and general blasting.
Slurry blasting agents	Al 0–35 Oxidizer* 50–80 H_2O 4–18 Other 0.2–10	1.1–1.6	2–6	0.7–2.0	Low (requires boosters)	Gelatin to thick or thin pea-soup consistency.	Large diameter, underwater, wet- and dry-hole blasting, large bombs.
Nitrostarch powders	Nitrostarch in place of NG	1.2	4–5	0.8–1.0	Moderately high, but less than dynamites	Good "fumes," fair water resistance, powerful, economical.	Small diameter blasting.
Composition B	40/59/1 TNT/RDX/wax	1.7	7.8	1.1	Average	Very high brisance.	Bursting charge and special weapons.
Composition B-3	40/60 TNT, RDX	1.73	7.9	1.15	High	Very high brisance.	Experimental standard.
Haleite or EDNA	$(CH_2NHNO_2)_2$	1.6 (pressed)	7.9	1.2	High	High brisance; less sensitive than RDX and PETN.	In Ednatols for bursting charges.
Ammonium picrate (Explosive D)	$(ONH_4)C_6H_2(NO_2)_3$	1.56 (pressed)	6.6	0.7	Very low	Insensitive to shock and friction, melts with decomposition, shells filled with high-pressure pressing	Armor-piercing shells.
Nitrostarch	Mixtures of various nitro esters of starch	1.4 (pressed)	6.4	0.95	High	Highly inflammable white powder	Demolition blocks and Trojan blasting explosives.
Tetryl	$(NO_2)_3C_6H_2CH_3N_2NO_2$	1.45 (pressed)	7.0	0.95	High	Very sensitive, rapidly reacting; easily pressed with 1–2% graphite, high brisance	Booster, base charge in caps; in tetrytols for bursting charges.
PETN (pentaerythritol tetranitrate)	$C(CH_2ONO_2)_4$	1.6 (pressed)	7.92	1.31	High	Very powerful and sensitive (more sensitive than RDX, less than NG).	In Primacord fuse; base charge in caps
Pentolite	50/50 TNT/PETN	1.63 (cast)	7.7	1.1	Moderate	High pressure or brisance; primacord sensitive	Booster and special weapons; commercial booster for prilled AN-fuel oil and slurry explosives.

(Continued)

Table B-2. (Continued) CHARACTERISTICS AND USES OF THE MORE IMPORTANT SECONDARY HIGH EXPLOSIVES

Name	Composition or Chemical Formula	Density (g/cc)	Detonation Velocity (km/sec)	Available Energy (kcal/g)	Sensitivity	Major Characteristics	Uses
Trinitrotoluene (TNT)	$CH_3C_6H_2(NO_2)_3$	1.59 (cast) 1.45 (pressed) 1.03 ("Pelletol") 0.8 (grained)	6.9 6.9 5.1 4.2	0.9 – – 0.8	Low	**Easily melted and cast; suitable liquid for slurrying with other explosives; easily pressed into blocks, completely waterproof.**	**Military; "Nitropel" TNT used in slurry explosives and in filling annulus between charge and borehole in water-filled holes; in amatols.**
Amatols	50/50 AN/TNT	1.55 (cast)	5–6.5 (depending on diameter)	0.95	Low	Insensitive; hygroscopic, not waterproof; less brisant but stronger than TNT; 50/50 can be cast; 80/20 either pressed or granulated.	Military, oil well shooting, quarrying; dry-hole booster for very low-sensitive types.
	80/20 AN/TNT	1.0 (loose) 1.45 (pressed)	4 (large diameter) 5.6 (large diameter)	0.93	Low		
Dinitrotoluene (DNT)	$CH_3C_6H_3(NO_2)_3$	1.28 (liquid) 0.8 (granular solid)	5 2–3.5 (depending on diameter)	0.7	Very low	Reddish brown or yellow liquid	Sensitizer in "Nitramons"; 60/40 NG/DNT in oil well shooting, up to 20% in TNT bursting charges, in FNH (flashless) propellant, 6% in small-arms ammunition (with guncotton)
Nitromethane (NM)	CH_3NO_2	1.12	6.2		Moderate	Clear, watery liquid	Special demolition, experimental studies of liquid explosives.
Cyclonite (RDX)	$C_3H_6N_6O_6$	1.2 (loose) 1.6 (pressed)	6.8 8.0	1.32	High	High thermal stability in solid state, expressively sensitive in pure state, 1.65 times as strong as low density TNT, 1.45 times as strong as cast TNT.	Major ingredient in plastic explosives, one of most brisant explosives in cast TNT (composition B), base charge in caps.
HMX	$C_4H_8N_8O_8$	1.89	9.1	1.35	High	Better than RDX in all respects	Same as RDX
HBX	Mixtures of RDX, TNT, aluminum, and wax	1.78	7.5	1.5	Average	Very powerful	Underwater explosive.
Plastic Explosives (Compositions A, C, C-2, C-3, C-4)	Waxed RDX	1.45–1.6	8.0	1.1–1.3	Moderate	Plastic, easily molded or pressed.	Specialized military demolition.
PBX 9404	94/3/ HMX/binder/ nitrocellulose	1.84	8.8	1.3	Moderate	Plastic bonded	Specialized military demolition.
Nitroglycerin (NG)	$C_3H_5(ONO_2)_3$	1.59	7.8	1.41	Very high (almost a primary explosive)	Oily, toxic liquid, volatile above 50°C, gelatinized by nitrocotton, exhibits low-order detonation with threshold priming.	Shooting oil wells, main explosive in dynamites, used in dynamites, used in double-base powders
Ethylene glycol dinitrate (EGDN)	$C_2H_4(ONO_2)_2$	1.48	7.4	1.43	Very high	Closely resembles NG, more volatile, toxic, slightly stronger but less brisant (owing to lower density)	**Used in solution with NG as freezing point depressant.**

(Continued)

Table B-2. (Continued) CHARACTERISTICS AND USES OF THE MORE IMPORTANT SECONDARY HIGH EXPLOSIVES

Name	Composition or Chemical Formula	Density (g/cc)	Detonation Velocity (km/sec)	Explosion Energy (kcal g)	Sensitivity	Major Characteristics	Uses
Straight dynamites[b]	20–60% NG, in balanced SN dope 20% grade ≡ 20% NG, etc.	1.3	4–6	0.55–0.85[b]	High	Cheesy, plastic substance; packed in paper cartridges, may be slit and tamped in borehole for greatest blasting effect; fired by detonator as are all dynamites; heat, friction, shock, and flame sensitive.	Ditching, stumping, other uses where high propagation-by-influence "sensitiveness" is required
Ammonia dynamites (and permissibles)	As above except NH_4NO_3 replaces part of NG and $NaNO_3$	0.8–1.2[b]	1.5–5.5 Depends on AN particle size, NG content.	0.7–0.9[b]	High	Cheaper than comparable grade straight dynamites; must be waterproofed by special additives	General small and large dynamite blasting, permissible (some grades)
Blasting gelatin	92:8 NG/nitrocotton ("Solidified" NG contains some wood pump to minimize low-order detonation)	1.55 (1.45)	7.5 (7.2)	1.45 (1.4)	High	Strongest, most brisant dynamite, completely waterproof, exhibits low-order detonation with threshold priming and under high pressures.	Oil well and submarine blasting, tunnel drilling, demolition.
Straight gelatin dynamite	20–90% grades	1.3–1.6[b]	4–7	0.75–1.15[b]	High	Jelly-like substance, powerful, waterproof, exhibits low-order detonation under threshold primering and high pressure.	In hard rock; mudcapping, demolition; submarine blasting.

[a]AN, SN, perchlorates, etc.

[b]Depends on grade.

"Reprinted from Reigel's Handbook of Industrial Chemistry, 7th Ed. James A. Kent, ed. Van Nostrand Reinhold, 1974.

Table B-3. CHARACTERISTICS AND USES OF THE MORE IMPORTANT PROPELLANTS (LOW EXPLOSIVES)

Name	Composition or Chemical Formula	Sensitivity	Major Characteristics	Important Uses
Colloidal nitrocellulose (N.C.) powders	Pyrocotton cellulose nitrate with 12.6% N	Low	Burning rate controlled by graining, hygroscopic, smokeless flame, with intense flash, gelatinized with alcohol-ethel.	Combined with stabilizers and modifiers to make smokeless powders for artillery, small arms, and sporting ammunition.
	Guncotton cellulose nitrate with 13.3% N		Pyrocotton and guncotton are usually blended to secure an average of 13.15% N.	Dry guncotton in fiber form is used in primers fired by an electric current
Double-base powders	60-80% Nitrocellulose. 20-40% Nitroglycerin	Moderate	Very rapid burning rate, controllable by surface area, mor powerful and more readily ignitable than straight N C. powders, causes erosion of gun bores, can be detonated and is subject to DDT.[d]	Propellant for mortars and sporting ammunition, not used by U.S armed forces as cannon powder because of bore erosion
Cordite	65% N.C., 30% NG, 5% vaseline	Low	Gelatinized with acetone	Propellant for large caliber naval guns (English).
FNH (Flashless nonhydroscopic powders)	Either straight N C. or double-base powders with addition of coolants, etc., to prevent muzzle flash, and decrease water absorption	Low	Like other smokeless powders, but can be rolled into sheets, flash reduced by DNT, potassium salts, etc	Propellant for small armor-piercing rockets such as the "Bazooka" (NG base); for naval ammunition (NG base).
Albanite, DINA powder	Di(2-nitrooxyethyl)nitramine	Low	Better flashless powder than FNH powders	Naval ammunition.
Rocket powder (solventless powder)	Nitrocellulose plasticized with about 50% NG, plus stabilizers and potassium salts	Low	Very rapid, uniform burning rate, can be made with thick section since no solvent need be removed.	For rockets up to 4 5 inches.
Chemical propellants[c]	Hydrogen peroxide, 80-90% H_2O_2 plus Ca, Na, or K permanganate (solid or aqueous solution).		Catalytic decomposition into water and O_2 releases about 1000 Btu per pound. Supplies oxygen to burn petroleum fuel	For driving turbines on submarines V-2 rocket-fuel pumps; jet motors, launching device for ram-jets.
	Hydrazine hydrate plus methyl alcohol.		Rapid combustion, fuel and oxidizer are both liquid.	For torpedo turbine drives.
	Fuming nitric acid-aniline.		Rapid rate of reaction generates heat and gases.	For launching device for ram-jets; jet motors.
	Mixed acid-monoethylaniline		As above.	As above.
	Liquid oxygen-kerosene.			Rocket motors.
Black powder	75% KNO_3 (or $NaNO_3$), 15% charcoal, 10% sulfur [example].	High	Cheap, excellent "heaving action," persistent smoky flame; very sensitive to friction, spark, and heat, hygroscopic.	Time (delay) fuses for blasting and shell; in igniter and primer assemblies for propellants; pyrotechnics; $NaNO_3$ powder, in commercial black powder and for practice bombs and saluting charges; (it is being discontinued as blasting charge).

[c]Many new rocket propellants have been described, the best ones are under security classifications
[d]DDT = deflagration to detonation transition.

APPENDIX C

PRODUCERS

Table C-1. MILITARY PRODUCERS OF EXPLOSIVE ORGANIC NITRATION PRODUCTS

Plant Name	Operating or[1] Managing Company	Location	Approx. Number of Employees	Estimated 1974 Sales ($Million)	Approx. Size of Plant	Product Line[2]	Description of Operations
Radford Army Ammunition Plant	Hercules, Inc.	Radford, Va. Montgomery County 24141 (703) 639-7631	>2000	70	4000 acres of manufacturing; 3000 acres of storage	TNT, NC, NG cannon & rocket	Coal-fired steam generators are employed to produce electricity. Nitric and sulfuric acids are made on site. Nitrocellulose is manufactured in a group of 12 continuous-feed reactors. Another twelve-reactor line is under construction. Current capacity is 5.4 Gg (12×10^6 lb) month. Two batch lines for production of nitroglycerine by the Biazzi method are available but not currently in operation.
Holston Army Ammunition Plant	Eastman Kodak Co., Inc.	Kingsport, Tenn. Sullivan County 37662 (615) 247-9111	1655	62	6525 acres	RDX, HMX	Nitric acid is produced on site. Two continuous and seven batch production lines are available for RDX production. HMX is produced in a continuous production line. Modernization is underway.
Volunteer Army Ammunition Plant	ICI America, Inc.	Chattanooga, Tenn. Hamilton County 37401 (615) 892-0115	515	33	7297 acres	TNT	Nitric and sulfuric acids are produced on site. The CIL continuous process is used. Process steam is produced but electricity is not. Red water is sold to local paper mills.
Joliet Army Ammunition Plant	Uniroyal, Inc.	Joliet, Ill Will County 60436 (815) 424-3221	500	90	N/A	TNT, Tetryl, DNT and primers	This plant is inactive, but rebuilding and moderization are underway. The CIL process was used for TNT production. Electricity is purchased from Commonwealth Edison of Chicago.
Badger Army Ammunition Plant	Olin Corp.	Baraboo, Wisconsin	N/A	N/A	N/A	NG, NC	This plant is inactive. Nitric and sulfuric acid production facilities are on site.
Sunflower Army Ammunition Plant	Hercules, Inc.	Lawrence, Kan. Johnson County 66018 (913) 843-3800	336	7	9522 acres	TNT	This plant is inactive. Rebuilding and modernization are underway.
Newport Army Ammunition Plant		Newport, Indiana Vermillion County 47966	N/A	N/A	N/A	TNT	This plant is inactive. Renovation is underway.

[1] This table describes government-owned, contractor-operated plants (GOCO) at which organic nitration reactions are conducted. The plants are owned by the U.S Army.

[2] **Abbreviations**

N/A	not available
NC	Nitrocellulose
NG	Nitroglycerine
RDX	Cyclotrimethylenetrinitramine
HMX	Cyclotetramethylenetetranitramine
TNT	Trinitrotoluene
Tetryl	Trinitrophenylmethylnitramine
DNT	Dinitrotoluene

Source: Nelson, T. P. and [illegible], Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry Radian Corp EAP Contract 68-02-1319, Task 50 July 1976

Table C-2. COMMERCIAL PRODUCERS OF EXPLOSIVE ORGANIC NITRATION PRODUCTS LISTED IN 1976 DIRECTORY OF CHEMICAL PRODUCERS

Company	Location	Product[1]
Air Products and Chems., Inc.	Pensacola, Fla.	DNT
Bofors America, Inc.	Linden, N.J.	PETN
E.I. duPont de Nemours & Co., Inc.		
Polymer Intermediates Dept.	DuPont, Wash.	NG
	Martinsburg, W.Va.	NG
	Louviers, Colo.	PETN
Organic Chems. Dept.		
Dyes and Chems. Div.	Deepwater, N.J.	DNT
Plastics Products and Resins Dept.	Carneys Point, N.J.	NC
Hercules, Inc.		
Indust. Systems Dept.		
Coatings & Specialty Products Dept.	Bessemer, Ala.	NG, PETN
	Parlin, M.J.	NC
Hummel Chem. Co., Inc.	South Plainfield, N.J.	Tetryl
Internat'l Minerals & Chem. Corp.		
Chem. Group		
Commercial Solvents Corp., subsid.		
Trojan-U.S. Powder Div.	Springville, Utah	RDX, PETN
	Seiple, Pa.	PETN
Olin Corp.		
Winchester-Western Div.		
Energy Systems Operations	East Alton, Ill.	RDX
Rubicon Chems., Inc.	Geismar, La.	DNT

[1]DNT Dinitrotoluene
PETN Pentaerythritol tetranitrate
NG Nitroglycerine
NC Nitrocellulose
Tetryl Trinitrophenylmethylnitramine
RDX Cyclotrimethylenetrinitramine

Source: Nelson, T.P. and R. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319 task 50. July 1976.

Table C-3. DESCRIPTIVE DATA ON COMMERCIAL PRODUCERS OF EXPLOSIVE ORGANIC NITRATION PRODUCTS

Plant Name	Operating or Managing Company	Owners	Location	Approx. Number of Employees	Estimated 1974 Sales ($Million)	Approx. Size of Plant	Product Line	Remarks
Apache Powder Co., Inc.	Apache Powder Co., Inc.	Apache Powder Co., Inc.	Benson, Ariz. Cochise County 85602 (602) 586-2217	225	9.0	640 acres	NG, NH_4NO_3 blending	Dynamite production capacity of 9 Gg/yr (20x10^6 lb/yr) is currently being phased out. Steam is produced on site and electricity is purchased.
Atlas Chemical Industries, Atlas Plant	Atlas Chemical Industries	ICI United States, Inc.	Webb City, Mo. Jasper County 64870 (417) 624-0212	500	2.4	1600 acres total	NG, NH_4NO_3, NH_4NO_3/fuel oil explosives (ANFO)	Steam is produced on site and electricity is purchased from Empire District Utilities of Joplin, Mo.
Austin Powder Co.	Austin Powder Co.	Austin Powder Co.	McArthur, On. Vinton County 45651 (614) 596-5286	400	22.1	1500 acres	NG and other explosives products such as blasting caps, fuses, etc.	The plant was built in 1930 and employs a batch process. Two coal-fired boilers are in operation.
E.I. duPont de Nemours Co.	E.I. duPont de Nemours Co.	E.I. duPont de Nemours Co.	Martinsburg, W.Va. Berkeley County 25401 (304) 267-3941	587	N/A	N/A	Dynamite, water gels, ANFO, smokeless powder	A batch process is employed for NG production. Oil-fired boilers produce process steam.
E.I. duPont de Nemours Co.	E.I. duPont de Nemours Co.	E.I. duPont de Nemours Co.	DuPont, Washington Pierce County 98327 (206) 584-1616	250-499	9	N/A	NG	This plant is permanently closed down and is used only for storage. DuPont is phasing out dynamite production.
duPont Polymers	E.I. duPont de Nemours Co.	E.I. duPont de Nemours Co.	Pompton Lakes, N.J. Passaic County 07442 (201) 835-1300	458	18.0	N/A	Lead Azide Lead Dinitro-Ortho-Cresol	Batch processes are employed. Process steam is produced by oil-fired boilers.
duPont Polymers	E.I. duPont de Nemours Co.	E.I. duPont de Nemours Co.	Carneys Point, N.J. Salem County 08069 (609) 299-4800	500-999	18.0	N/A	NC	
Hercules, Inc.	Hercules, Inc.	Hercules, Inc.	Port Ewen, N.Y. Ulster County 12466 (716) 338-2144	500-999	18.4	N/A	Blasting caps, NC	Nitric acid is purchased. Electric power is produced on site with an oil-fired boiler. The nitrocellulose produced is not explosive grade. It is sold to the lacquer/paint industry.
Hercules, Inc.	Hercules, Inc.	Hercules, Inc.	Kenvil, N.J. Morris County 07847 (201) 366-5150	For Kenvil, Carthage & Bessemer plants - total <500	17.7	Extensive acreage	NG	Nitric acid is purchased and power is produced on site.

(Continued)

Table C-3. (Continued) DESCRIPTIVE DATA ON COMMERCIAL PRODUCERS OF EXPLOSIVE ORGANIC NITRATION PRODUCTS

Plant Name	Operating or Managing Company	Owners	Location	Approx. Number of Employees	Estimated 1974 Sales ($Million)	Approx. Size of Plant	Product Line	Remarks
Hercules, Inc.	Hercules, Inc.	Hercules, Inc.	Carthage, Mo. Jasper County 64836 (417) 358-4061	For Kenvil & Bessemer plants - total <500 Carthage - 150	6.0	Extensive acreage	NG	Nitric acid is purchased and power is produced on site.
Hercules, Inc.	Hercules, Inc.	Hercules, Inc.	Bessemer, Al. Jefferson County 35020 (205) 428-2391	For Kenvil & Bessemer plants - total <500	6.0	Extensive acreage	NG	A recent explosion has stopped production. An operating nitric acid plant is present. Rebuilding and conversion to the Biazzi process are underway.
Hercules, Inc. Pluto Plant	Hercules, Inc.	Hercules, Inc.	Ishpeming, Mich. Marquette County 49849 (906) 486-9202	20-49	1.2	N/A	N/A	
Olin Matheison Corp.	Olin Matheison Corp.	Olin Corp.	St. Marks, Fla. Wakulla County 32355 (904) 925-6131	50-99 4 people directly involved in NG production.	2.7	The NG plant is only 400 x 600 ft.	NG propellant	The Nitro-Nobel process is employed. Electricity is purchased from Florida Light and Power. Steam is produced on site.
Trojan-U.S. Powder	Trojan-U.S. Powder	Commercial Solvents Corp.	Spanish Fork, UT. 84660 (801) 489-5644	95 total	proprietary	N/A	PETN, RDX, formulated products	Proprietary processes are employed. Steam is produced on site.

Source: Nelson, T.P. and R. Pyle. Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319 task 50. July 1976.

Table C-4. DESCRIPTIVE DATA FOR ADDITIONAL COMMERCIAL ESTABLISHMENTS CLASSIFIED IN SIC 2892

Plant Name	Operating or Managing Company	Owners	Location	Approx. Number of Employees	Estimated 1974 Sales ($Million)	Approx. Size of Plant	Product Line	Comments
Austin Powder Co.	Austin Powder Co.	Austin Powder Co.	Glenwillow, Oh. Cuyahoga County 44139 (212) 232-0600	50-99	1.5	N/A	N/A	
Austin Powder Co.	Austin Powder Co.	Austin Powder Co.	Madisonville, Ky. 42431 (502) 821-5340	N/A	0.8	N/A	N/A	
Centennial Division VWR	Centennial Division VWR	Univar Corp.	Brisbane, Ca. San Mateo County 94005 (415) 469-0100	250-499	7.5	N/A	Wholesale distribution only, no maunfacturing	
Dow Chemical Co.	Dow Chemical Co.	Dow Chemical Co.	Biwabik, Minn. St. Louis County 55708 (218) 865-6301	20-49	0.9	N/A	NH_4NO_3 blending only	No nitration processes
DuPont Polymers	E.I. duPont de Nemours Co.	E.I. duPont de Nemours Co.	Seneca, Ill. LaSalle County 61360 (815) 357-8711	245	3.8	N/A	Water gels	Batch processes. Oil-fired boilers for process and heating steam.
E.I. duPont de Nemours Co.	E.I. duPont de Nemours Co.	E.I. duPont de Nemours Co.	Watson, Alabama Jefferson County 35181 (205) 674-9436	88	N/A	N/A	Water gels, ANFO	Batch processes. Oil-fired boilers for process and heating steam.
Ensign Bickford Co.	Ensign Bickford Co.	Ensign Bickford Co.	Louviers, Col. Douglas County 80131 (303) 798-8625	50-99	3.0	N/A	Manufacture explosive fuses	No nitration processes.
Explosive Technology	Explosive Technology	Explosive Technology	Fairfield, Ca. Goland County 94533 (707) 422-1880	100-249	4.5	N/A	N/A	
Gearhart-Owen Ind.	Gearhart-Owen Ind.	Gearhart-Owen Ind.	Ft. Worth, Tx. Tarrant County 76101 (817) 293-1300	N/A	8.8	N/A	N/A	
Harrison Jet Guns, Inc.	Harrison Jet Guns, Inc.	Harrison Jet Guns, Inc.	Ft. Worth, Tx. Tarrant County 76119 (817) 478-9216	20-49	0.9	N/A	Propellants	No nitration processes.
Hercules, Inc.	Hercules, Inc.	Hercules, Inc.	Research Triangle Park, N.C. Durham County 27709 (919) 549-8271	50-99	2.4	N/A	N/A	

(Continued)

Table C-4. (Continued) DESCRIPTIVE DATA FOR ADDITIONAL COMMERCIAL ESTABLISHMENTS CLASSIFIED IN SIC 2892

Plant Name	Operating or Managing Company	Owners	Location	Approx. Number of Employees	Estimated 1974 Sales ($Million)	Approx. Size of Plant	Product Line	Comments
Hercules, Inc.	Hercules, Inc.	Hercules, Inc.	Virginia, Minn. St. Louis County 55792 (218) 749-1501	20-49	0.9	N/A	N/A	
Holex, Inc.	Holex, Inc.	Holex, Inc.	Hollister, Ca. San Benito County 95023 (408) 637-5851	50-99	2.7	N/A	Manufacture electo-explosive components	
Ireco Chemical, Inc.	Ireco Chemical, Inc.	Ireco Chemical, Inc.	Lehi, Utah Utah County 84043 (801) 768-2801	20-49	0.9	N/A	NH_4NO_3 blending 1-3 million lbs/yr of blended explosives	No nitration processes.
Ireco Chemical, Inc.	Ireco Chemical, Inc.	Ireco Chemical, Inc.	Salt Lake City, Utah Salt Lake County 84119 (801) 521-2890	50-99	1.5	N/A	NH_4NO_3 blending; no manufacturing, make slurry explosives from NH_4NO_3	No nitration processes.
Ireco Chemical, Inc.	Ireco Chemical, Inc.	Ireco Chemical, Inc.	Jordan, Utah Salt Lake County 84084 (801) 255-6801	50-99	1.5	N/A	NH_4NO_3 blending; no manufacturing, make slurry explosives from NH_4NO_3	No nitration processes.
Jet Research Center, Inc.	Jet Research Center, Inc.	Halliburton Co.	Arlington, Tx. Tarrant County 76010 (817) 275-2864	100-249	4.5	N/A	Blasting caps, etc.	No nitration processes.
McCormick Selph	McCormick Selph	Teledyne Inc.	Hollister, Ca. San Benito County 95023 (408) 637-3731	250-499	7.5	N/A	NH_4NO_3 blending, blending explosives	No nitration processes.
Mesabi Blasting Agents, Inc.	Mesabi Blasting Agents, Inc.	Ireco Chemicals Inc.	Biwabik, Minn. St. Louis County 55708 (218) 865-6366	20-49	0.9	N/A	NH_4NO_3 blending only	No nitration processes.
Monsanto Co.	Monsanto Co.	Monsanto Co.	Bonne Terre, Mo. Saint Francois Co. 63628 (314) 756-5757	17	0.6	720 acres total plant acreage <1 acre	NH_4NO_3 blending only	No nitration processes, just blending.
National Powder Co., Inc.	National Powder Co., Inc.	National Powder Co., Inc.	Eldred, Pa. McKean County 16731 (814) 225-4701	50-99	2.1	N/A	N/A	
Olin Mathieson Chemical	Olin Mathieson Chemical	Olin Corp.	Peru, Ind. 46970 (317) 473-5571	N/A	1.4	N/A	N/A	
Olin Energy Systems	Olin Energy Systems	Olin Corp.	Marion, Ill. Williamson County 62959 (618) 985-3721	500-999	15.0	N/A	NH_4NO_3 blending	No nitration processes.

(Continued)

Table C-4. (Continued) DESCRIPTIVE DATA FOR ADDITIONAL COMMERCIAL ESTABLISHMENTS CLASSIFIED IN SIC 2892

Plant Name	Operating or Managing Company	Owners	Location	Approx. Number of Employees	Estimated 1974 Sales ($Million)	Approx. Size of Plant	Product Line	Comments
Space Ordinance Systems Division	Space Ordinance Systems, Inc.	Transtechnology Co.	Sunnyvale, Ca. Santa Clara County 94086 (408) 736-9060	100-249	3.0	N/A	N/A	
Specialty Chemicals, ICI U.S.	Specialty Chemicals, ICI U.S.	Specialty Chemicals, ICI U.S.	Joplin, Mo. Jasper County 64801 (417) 624-0212	N/A	13.8	N/A	N/A	
Technical Ordinance, Inc.	Technical Ordinance, Inc.	Technical Ordinance, Inc.	Minneapolis, Minn. Hennepin County 55426 (612) 925-2822	50-99	1.5	N/A	Use explosives; no manufacturing	Apparently a blasting company that uses explosives.
Titan Explosives Co.	Titan Explosives Co.	Titan Explosives Co.	Milwaukee, Or. Clackamas County 97222 (503) 632-2952	50-99	1.5	N/A	Nitro carbon, nitrate explosive & NH_4NO_3 blends	
Univar Corp.	Univar Corp.	Univar Corp.	Seattle, Wash. 98104 (206) 447-5911	N/A	7.0	N/A	N/A	Apparently this plant is permanently inactive, but may be used for storage.
Whittaker Corp.	Whittaker Corp.	Whittaker Corp.	N. Hollywood, Ca. Los Angeles County 91605 (213) 764-2780	50-99	2.1	N/A	N/A	Propellant research center.

Source: Nelson, T.P. and R. Pyle Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry. Radian Corp. EPA Contract 68-02-1319 task 50. July 1976.

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16. ABSTRACT

The catalog of Industrial Process Profiles for Environmental Use was developed as an aid in defining the environmental impacts of industrial activity in the United States. Entries for each industry are in consistent format and form separate chapters of the study. The explosives industry as a whole includes companies which manufacture organic nitration products and formulate mixtures of chemicals with explosive properties. Five nitration processes are described along with the process for production of nitric acid used in the nitration reactions. Six process flow charts and fifteen process descriptions have been prepared to characterize the industry. Within each process description available data have been presented on input materials, operating parameters, utility requirements and waste streams. Data related to the subject matter, including company, product and raw material data, are included as appendices.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Air Pollution Control	07B
Explosives	Water Pollution Control	13C
Organic Nitrates	Solid Waste Control	19D
Nitric Acid	Explosive Disposal	19A
Nitration Reaction		
Munitions		
Pyrotechnics		
Process Description		

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